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ACTIVATION ENERGY OF THERMAL DECOMPOSITION OF SmC_2O_4Cl TO SmOCl, CO AND CO_2

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An activation energy of E_a = 213.73 kJ mol^{-1} has been determined for the thermal decomposition of SmC_2O_4Cl to SmOCl, CO and CO_2. The result is predictable on the basis of the Kahwa-Mulokozi expression+ for the activation energy and its extended interpretation.

The basis for our mechanistic interpretation of the thermal decomposition kinetics of oxalate is the Kahwa-Mulokozi expression for the activation energy [1,2]:

$$E_a = 127 + 1.4853 \times 10^{-6} (I_T^2 - 9800)^2$$

where the ionization potential term $I_T = r_c / r_i (\sum I)^{1/2}$ is defined by Pauling's covalent radius r_c [3], ionic radius r^i in hexacoordination, and the sum of the ionization potentials $\sum I$ of the metalatom.

\+ See ref.2

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In this study, the ionic radii according to Shanon and Prewitt [4] and the ionization potentials according to Factor and Hanks [5] have been used. Further, the chemical data compilation due to Aylward and Findlay [6] has been utilized.

The thermal decomposition pathways under consideration are

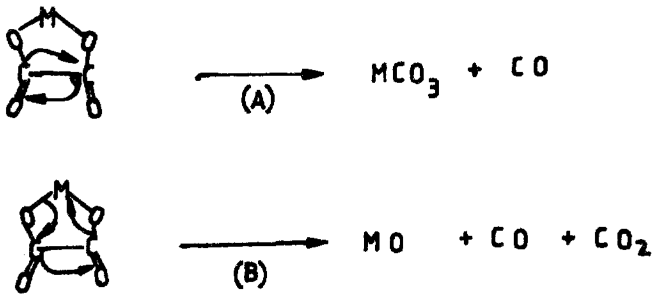
$$MC_2O_4 \rightarrow MCO_3 + CO \quad (1)$$

and

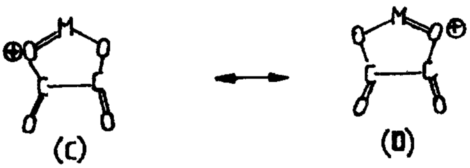
$$MC_2O_4 \rightarrow MO + CO + CO_2 \quad (2)$$

Mechanistically, expression (i) is accounted for by a rate-determining step in which breaking of the C-O_I and M-O_I bonds features prominently [7].

The C-O_I bond, which has the maximum multiplicity (1.5) at $I_T^2 = 0$), becomes progressively weaker as I_T increases. The increasing electrostatic interaction promotes an increasingly closer approach of the acceptor and donor orbitals for effective overlap and the formation of a covalent M-O_I bond. A consequence of the resulting increasing drift of electrons from the oxalate to the metal atom is a progressive decrease in the C-O_I bond multiplicity. As the covalence of M-O_I increases, the breaking of the C-O_I bond continues to be significant in the rate-determinating step until the two bonds are energetically equivalent. The activation energy for the thermal decomposition of oxalate therefore decreases progressively towards the minimum



value (127 kJ mol^{-1}), at I_T^2= 9800, where (1) and (2) should occur with equal probability, according to (A) and (B):



On further increase of I_T the multiplicity of M-O_I increases and the resonance structures become increasingly significant. The mechanism is therefore shifted squarely in favour of (B) and the activation energy assumes an increasing trend.

Study of the thermal decomposition kinetics of the lanthanide oxalato complexes LnC_2O_4Cl affords an excellent opportunity to test the arguments which we have used to interpret (i). Since the resonance structures (C) and (D) reduce the electrophilicity of the cation with respect to its interaction with other ligands, a strong covalent metal-oxalate bond is not compatible with the presence of a strong donor in the coordination polyhedron. On the other hand, a weak donor gives a minimum increase in electron density on the cation, which favours the resonance structures (C) and (D). This argument explains the increase in the activation energy from 127 kJ mol^{-1} in $Nd_2(C_2O_4)_3$ to 195 kJ mol^{-1} in NdC_2O_4Cl [7].

This increase in the activation energy appears surprisingly large, and it stimulated us to study the thermal decomposition kinetics of other oxalato complexes. Our choice of $SmC_2O_4Cl.3H_2O$ for study offers an opportunity to investigate the combined effect of a weak donor and the increase in the value of the ionization potential term from 99.96 (Nd) to 107.66 (Sm).

In the present study, an activation energy of E_a = 213.73 kJ mol^{-1} is obtained for the thermal decomposition of SmC_2O_4Cl to SmOCl, CO and CO_2. The result is shown by a model calculation to be realistic.

Experimental

A Stanton Redcroft TG 750 thermal balance was used for the stud of the thermal decomposition kinetics of oxalate according to the isoconversional method. The procedure and details of the method of preparation of $SmC_2O_4Cl.3H_2O$ are as described in our previous work on $NdC_2O_4Cl.3H_2O$ [7].

Results and discussion

The TG curve of $SmC_2O_4Cl.3H_2O$ is shown in Fig. 1. In its main features, the thermogravimetry of $SmC_2O_4Cl.3H_2O$ (72 mg, heating rate 10 deg/min, and atmosphere of dry N_2 flowing at 25 ml/min) resembles that of $NdC_2O_4Cl.3H_2O$ [7]. A small amount of coordinated water ($\approx$ 10%) is retained until the start of the thermal decomposition of oxalate. As will be explained, this affects the thermal decomposition kinetics considerably at degrees of conversion up to $\alpha = 0.1$.

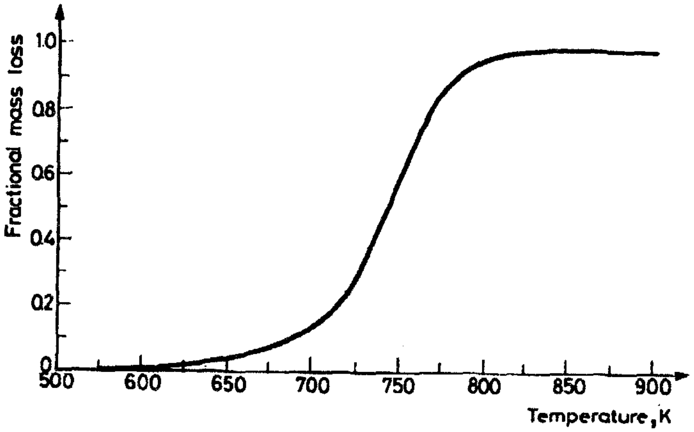


Fig. 1 Thermogravimetry of $SmC_2O_4Cl. 3H_2O$ at a heating rate of 10 deg /min

As in the previous study [7], the kinetic data (Table 1) were evaluated via the equation

$$\log\beta / T^2 [1 - 2!/(E/RT) + 3!/(E/RT)^2 \ldots] =$$

$$= -E/2.303RT + \log AR/Eg(\alpha)$$

whereby the asymptotic expansion in E/RT is achieved in an iterative computer program. The respective Arrhenius plots (Fig. 2) give

$$\log\beta_i / T_i^2 [1 - 2!/(E/RT_i \ldots] \text{vs.} 1/T_i$$

where, for a chosen degree of conversion α_i, β_i and T_i are the heating rate and temperature, respectively.

Table 1 Kinetic data on the thermal decomposition of SmC_2O_4Cl to $SmOCl$, CO and CO_2

Deggree of conversion α	Temperatures T_i K for various heating rates, deg/min 1	2	3	5	10	Activation energy, kJ/mol^{-1}
0.1	678.47	685.42	702.00	714.06	724.50	171.53
0.2	700.17	714.06	723.50	732.29	743.75	214.50
0.3	710.59	726.22	735.00	743.58	757.00	211.02
0.4	720.83	733.16	745.00	752.50	767.00	214.09
0.5	727.95	740.10	752.50	760.94	775.00	212.74
0.6	753.76	749.31	760.00	769.62	785.00	210.99
0.7	743.58	757.47	765.50	778.30	793.25	212.90
0.8	753.82	766.15	777.50	788.72	805.00	210.45
0.9	768.75	779.17	791.25	800.87	818.75	223.16

As shown by the data in Table 1 and the Arrhenius plots (Fig. 2), the reaction is mechanistically uniform between $\alpha = 0.2$ and $\alpha = 0.9$. The value of the activation energy at $\alpha = 0.1$ is 171.53 kJ mol^{-1}, while the average value of the activation energy for α between 0.2 and 0.9 is 213.73 kJ mol^{-1}.

On the basis of a comparison of the infrared spectra of $Ln_2(C_2O_4)_3.10H_2O$ and $LnC_2O_4Cl.3H_2O$, a strengthening of the M-O$_I$ bond by Cl^- is shown by the positions of the v(M-O) vibrational mode. The v(M-O) mode observed between 490 and 500 cm^{-1} in the oxalate hydrates [8,9] was shown by a theoretical band assignment according to normal coordinate analysis to be strongly coupled with the deformation vibrations: 38% δ(O-C-O) + 32% δ(C-O-M) + 20% v(M-O) + 10% δ(O-M-O) in $Sm_2(C_2O_4)_3.5H_2O$ [10]. In $NdC_2O_4Cl.3H_2O$ and $SmC_2O_4Cl.3H_2O$ the band is split to give pairs observed at 467 and 513 cm^{-1} and 467 and 520 cm^{-1}, respectively (Fig. 3). The splitting of the band is due to the presence of non-equivalent oxalate ligands in the coordination polyhedron. This is because the enhancement of the electrophilicity of the cation by a weak donor is greater in the trans position. Accordingly, a stronger M-O_I bond is given by the trans oxalate and a weaker one by the oxalate closest to the chloride.

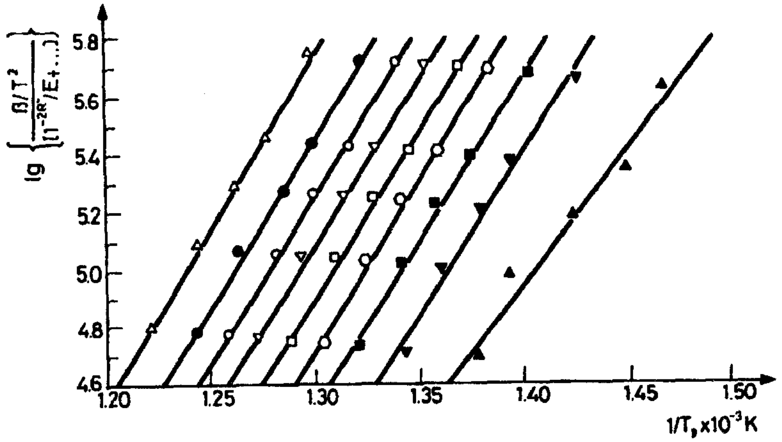


Fig. 2 Arrhenius plots for evaluation of kinetic measurements of SmC_2O_4Cl according to the isoconversional method

Thermoanalytically, there are also two distinguishable oxalate ligands. Up to $\alpha = 0.1$, the thermal decomposition of oxalate occurs simultaneously with the expulsion of the residual water of coordination (10%), probably involving $LnC_2O_4Cl.3H_2O$. The low value of the activation energy obtained speaks for the lowering of the electrophilicity of the cation as a result of electron donation by the water molecules. Above $\alpha = 0.1$, all the water has been expelled, and the electrophilicity of the cation increases, with resulting increase in the covalent strength of the M-O_I bond. The thermal decomposition of oxalate therefore proceeds with a higher activation energy value.

According to our theoretical approach, the activation energy at $I^2_T > 9800$ is determined by the covalent strength of the M-O_I bond. Thus, as a result of the modifying influence of the other ligands on the chemical environment in the coordination polyhedron, a quantitative prediction of the variation in the activation energy requires a quantitative definition of the bond strength.

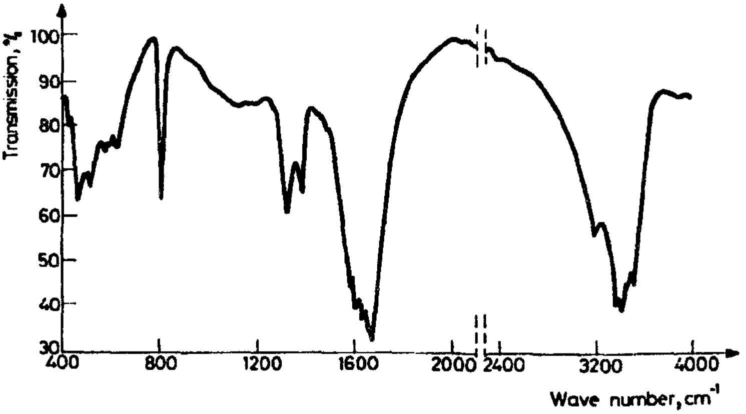


Fig. 3 Infrared spectrum of $SmC_2O_4Cl.\ 3H_2O$

If γ is the covalent strength of Ln-Cl relative to the strength of the single bond M-O_I (in $Ln_2(C_2O_4)_3$ at $I_T^2 = 9800$), the M-O_I bond strength in LnC_2O_4Cl will be $3/2(1+\gamma)$ times as strong as that in the respective oxalate. Numerically, the ratio cannot be equal to the ratio of the activation energies. This is because the bond energies refer to the ground states, while the activation energies refer to the excited states. Significantly, a decomposing oxalate ligand is in vibrational motion. The ratio of the bond strengths must therefore be equal to the ratio of the values of (E_a + E_v), where E_v is the vibrational energy for the stretching and deformation of the M-O_I and C-O_I bonds. Accordingly, we obtain;

$$E'_a + E'_v = 3/2(1+\gamma)(E_a + E_v)$$

As we have already seen the coupling of v(M-O_I) with the deformation vibrations gives a band near 490 cm^{-1} for the lanthanide oxalates. The predominantly v(C=O) stretching mode 75% v(C-O) + 20% δ(O-C-O) +5% δ(C-O-M) is found at 1320 cm^{-1} in the infrared spectrum of $Sm_2(C_2O_4)_3.5H_2O$ [10]. For a single M-O_I bond, the nearest oxalate with $I_T^2 = 9800$ is neodymium oxalate. For this compound, E_v = 21.64 kJ mol^{-1}; for $NdC_2O_4Cl.3H_2O$, E'_v = 21.97 kJ mol^{-1}. Using the activation energies E_a = 127 kJ mol^{-1} and E'_a = 195 kJ mol^{-1}, we obtain the value of the ratio $3/2(1+\gamma) = 1.4597$ and $\gamma = 2.76\%$. This calculation shows Cl^- to be a weak donor, which is again demonstrated by the agreement between the approximate value obtained by putting γ =0: E_a = 200.99 kJ mol^{-1} and the experimental value of E_a = 195 kJ mol^{-1}.

In the oxalates, the covalence of the M-O$_I$ bond is increased, corresponding to the increase in the value of the ionization potential term from 99.96 to 107.66. The increase in the activation energy is 4.76 kJ mol^{-1}, which gives a fractional increase $4.76/(E_a + E_v) = 0.03206$. The ratio of the bond strengths is therefore increased to 1.03206 x 1.4597 = 1.5065. The activation energy E_a = 131.76 is calculated according to (i); E_v = 21.71 kJ mol^{-1} corresponds to ν_{10} = 495 cm^{-1} and ν_{11} = 1320 cm^{-1} in the infrared spectrum of $Sm_2(C_2O_4).5H_2O$, and E'_v = 22.00 kJ mol^{-1} is given by ν_{10} = 520 cm^{-1} and ν_{11} = 1325 cm^{-1} in the infrared spectrum of $SmC_2O_4Cl.3H_2O$. The activation energy E'_a = 209.2 kJ mol^{-1} is obtained, in good agreement with the experimental value.

Conclusion

In the present study, application of the Kahwa-Mulokozi expression to the activation energy of the thermal decomposition of this oxalate was used to expose the correspondence between bonding and thermal decomposition properties. The approach is unprecedented in giving access to comprehensive information on chemical bonding via a technique of thermal analysis.

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Zusammenfassung - Für den thermischen Zerfall von SmC_2O_4Cl in $SmOCl$, CO und CO_2 wurde eine Aktivierungsenergie von E_a = 213.73 $kJ.mol^{-1}$ ermittelt. Dieses Ergebnis kann auf der Basis der Kahwa-Mulokozi-Beziehung[+] für die Aktivierungsenergie und ihrer erweiterten Interpretation vorhergesagt werden.