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THE MECHANISM OF THERMAL DECOMPOSITION OF IONIC OXALATES

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A mechanism for the thermal decomposition of ionic oxalates has been proposed on the basis of three quantitative relationships linking the quantities r_c/r_i (the ratio of the Pauling covalent radius and the cation radius of the metal atom in hexacoordination) and ΣI_i (the sum of the ionization potentials of the metal atom in kJ mol^{-1}) with the onset oxalate decomposition temperature (T_d) (Eq. 1) the average C—C bond distance ($\bar{d}$) (Eq. 2), and the activation energy of oxalate decomposition (E_a) (Eq. 3):

$$T_d = 516 - 1.4006 \frac{r_c}{r_i} (\Sigma I_i)^{\frac{1}{2}} \tag{1}$$

$$\bar{d} = 1.527 + 5.553 \times 10^{-6} \left(122 - \frac{r_c}{r_i} (\Sigma I_i)^{\frac{1}{2}}\right)^2 \tag{2}$$

$$E_a = 127 + 1.4853 \times 10^{-6} \left(\left(\frac{r_c}{r_i}\right)^2 \Sigma I_i - 9800\right)^2 \tag{3}$$

On the basis of these results it is proposed that the thermal decomposition of ionic oxalates follows a mechanism in which the C—O bond ruptures first. From Eq. 3 it is further proposed that strong mutual electronic interactions between the oxalate and the cations restrict the essential electronic reorganization leading to the products, thereby increasing E_a.

In our previous contribution [1] we reported a quantitative expression (Eq. 1) linking the quantities r_c/r_i (the ratio of the Pauling covalent radius [2] and the ionic radius of the metal atom in hexacoordination [3]) and ΣI_i (the sum of the ionization potentials of the metal atom in kJ mol^{-1} [4, 6]) with the onset oxalate decomposition temperatures (T_d):

$$T_d = 516 - 1.4006 \frac{r_c}{r_i} (\Sigma I_i)^{\frac{1}{2}} \tag{1}$$

Equation 1 identifies mutual electronic interactions between the cation and the oxalate anions as ranking high in importance among the factors bearing on the oxalate decomposition process. The influence of these electronic interactions on

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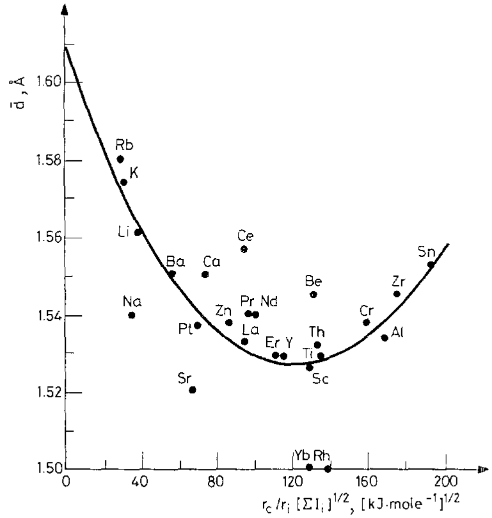


Fig. 1. The average C—C bond distance (*d*) of some metal oxalates and oxalatometallates *vs.* the ratio $\frac{r_c}{r_i}(\Sigma I_i)^{\frac{1}{2}}$

Table 1

The experimental average carbon-carbon bond ($\bar{d}$) in some metal oxalates and oxalatometallate anions

Compound	$\bar{d}$, Å	Ref.	Compound	$\bar{d}$, Å	Ref.
$M_2C_2O_4 \cdot n\,H_2O$			M = Ce	1.557 (70)	16
M=Li	1.561 (4)	5	Pr	1.540 (50)	16
Na	1.54 (7)	7	Nd	1.540 (40)	17
K	1.574 (24)	8	Yb	1.50 (4)	18
Rb	1.58 (4)	9	Sc	1.526 (15)	19
$MC_2O_4 \cdot 2\,H_2O$			$M(C_2O_4)_2^{2-}$		
M = Ca	1.55 (2)	10	M = Be	1.545 (3)	20
Sr	1.52 (4)	12	Cu	1.565 (?)	21
Ba	1.55 (2)	11	Pt	1.537 (40)	22
$\alpha-MC_2O_4 \cdot 2\,H_2O$			Mn	1.564 (18)	23
M = Mn	1.593 (35)	13	$M(C_2O_4)_2^-$		
Fe	1.65 (5)	14	M = Ti	1.529 (6)	24
Co	1.416 (35)	13	Y	1.529 (26)	25
Ni	1.331 (35)	13	Er	1.529 (11)	26
Zn	1.538 (35)	13	$M(C_2O_4)_3^{3-}$		
$\alpha-CuC_2O_4 \cdot 2\,NH_3$	1.481 (30)	15	M = Al	1.534 (9)	26
$\beta-MC_2O_4 \cdot 2\,H_2O$			Cr	1.538 (4)	27
M = Fe	1.27 (5)	14	Rh	1.495 (?)	28
Co	1.343 (35)	13	$M(C_2O_4)_4^{4-}$		
Ni	1.320 (35)	13	M = Sn	1.553 (8)	29
$M_2(C_2O_4)_3 \cdot n\,H_2O$			Th	1.532 (?)	30
M = La	1.533 (30)	16	Zr	1.545 (8)	31

the bonding in the oxalate anion is found to be critical, as indicated by the quantitative expression (Eq. 2) which reproduces the average C–C bond distances (d) in oxalates and oxaltometallate anions:

$$\bar{d} = 1.527 + 5.553 \times 10^{-6} \left(122 - \frac{r_c}{r_i} (\Sigma I_i)^{\frac{1}{2}}\right)^2 \tag{2}$$

Furthermore, the limitations encountered in a comparative interpretation of the kinetics of topochemical processes notwithstanding, a definite trend (Eq. 3) appears to be followed when the activation energies of oxalate decomposition (E_a) are correlated with the ratio $\left(\frac{r_c}{r_i}\right)^2 \Sigma I_i$:

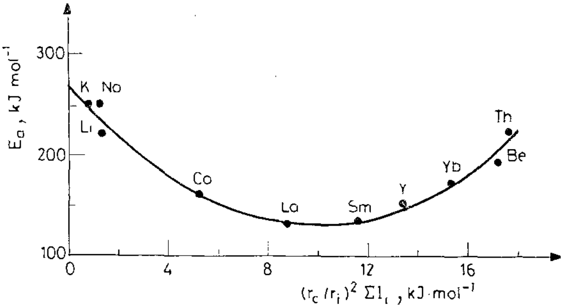


Fig. 2. Activation energy of metal oxalate decomposition *vs.* the ratio $\left[\frac{r_c}{r_i}\right]^2 \Sigma I_i$

$$E_a = 127 + 1.4853 \times 10^{-6} \left[\left(\frac{r_c}{r_i}\right)^2 \Sigma I_i - 9800\right]^2 \tag{3}$$

On the basis of these complementary results (Eqs 1–3), it has been possible to make proposals regarding the oxalate decomposition mechanism with reasonable justification. The results in Eqs 1–3 have been interpreted, and an oxalate decomposition mechanism which is consistent with the interpretation put forward is proposed.

Experimental

The oxalate decomposition temperatures referred to in the text are those reported in our earlier study [1]. The experimental C–C distance ($\bar{d}$) is the average of all the C–C bond distances reported in the respective structure determinations (Table 1 and Fig. 1). The activation energies (E_a) used to obtain Fig. 2 are those determined for oxalate decomposition employing metallic crucibles. Subsequently, other activation energies which agreed closely with the established trend were included.

Table 2

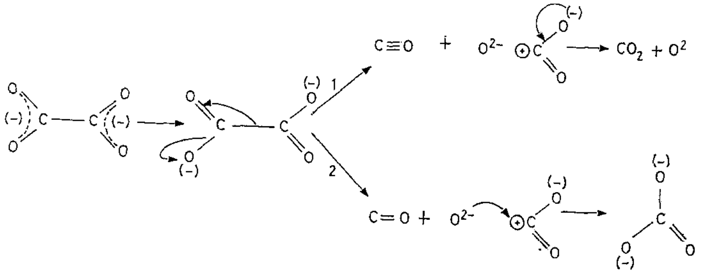
The activation energies of oxalate decomposition

Metal oxalate	E_a, kJ mol^{-1}	Crucible material or decomposition medium	Heating rate/ programme, °C/min	Atmosphere	Sample weight, mg	Reference
$M_2C_2O_4$						
M = Li	220	Platinum	Isothermal	dry nitrogen	100	33
Na	250	KBr matrix	Isothermal	—	4 mg/g of KBr	34
K	250	KBr matrix	Isothermal	—	4 mg/g of KBr	34
MC_2O_4						
M = Be	190	?	Isothermal	?	100	35
Ca	160	Platinum	10	air	35	36
$M_2(C_2O_4)_3$						
M = La	130	Silver	Isothermal	Vacuum	5–17	37
Sm	130	?	?	Vacuum/air	?	38
Yb	170	Silver	Isothermal	Vacuum	6–8	39
Y	150	Silver	Isothermal	Vacuum	6–9	40
Pu	150	Platinum	10	air	35	36
$M(C_2O_4)_2$						
M = Th	220	Platinum	10	air	35	36
	225	Platinum	6	air	500	41

Results and discussion

A plot of $\bar{d}$ *vs.* the ratio $\frac{r_c}{r_i}(\Sigma I_i)^{\frac{1}{2}}$ (Fig. 1) is parabolic and deviations are observed where large errors are reported in structural determinations. The carboxylate groups apparently experience the largest mutual repulsion when their electronic interactions with the cations are minimum; hence the largest value of $\bar{d}$ = 1.610 Å is predicted for $r_c/r_i(\Sigma I_i)^{\frac{1}{2}} = 0$. Increments in the electronic interactions between the oxalate group and the cations are expected to reduce the electron density in the carboxylate groups, thereby reducing the repulsion between them. This factor is found to manifest itself in the contraction of the C–C bond as the ratio $r_c/r_i(\Sigma I_i)^{\frac{1}{2}}$ increases to 122. However, beyond this value the mutual electronic interactions appear to be sufficiently high to cause an electron drift from the C–C bond. For this reason, the minimum value of 1.527 Å is obtained, instead of the value 1.504 Å which is considered to be normal for the $C_{sp^2} - C_{sp^2}$ bond [32]. Due to extensive electronic interactions between the metal atom and the oxalate group through the 3d-orbitals, the trend adopted by the $\bar{d}$ values in transition metal oxalates deviates markedly from the one found in ionic oxalates (Table 1).

On the basis of the trend shown by the onset decomposition temperatures (Eq. 1) and the electronic distribution inferable from structural data (Eq. 2), it is proposed that oxalate decomposition follows a mechanism in which the C–O bond ruptures first. Rupture of the C–O bond may be followed by electronic reorganization leading to either C≡O, CO_2 and O^{2-} (route 1) or C≡O and CO_3^{2-} (route 2), as follows:



Evidence in support of the mechanism proposed above is found in the plot of the activation energy (E_a) of oxalate decomposition vs. the ratio $\left(\frac{r_c}{r_i}\right)^2 \Sigma I_i$ in Fig. 2. When the oxalate anion is most stabilized by resonance, the C–O bond is strongest, and accordingly the oxalate decomposition temperature and activation energy are highest (Eqs 1 and 3). Large mutual electronic interactions between the carboxylate groups and the cations weaken the C–O bond, thereby lowering the decomposition temperature and the activation energy (Eqs 1 and 3). However, the occurrence of a minimum point in Fig. 2 indicates that strong mutual electronic interactions between the cations and the oxalate anions restrict the electronic reorganization leading to the products. Accordingly, this electronic reorganization assumes prominence in the course of the oxalate decomposition process when the ionic potential $\frac{r_c}{r_i}(\Sigma I_i)^{\frac{1}{2}}$ is large and correspondingly increasing values of E_a are observed. Route 1 is favoured when the oxalate group is attached to a cation of large ionic potential while route 2 is favoured when the ionic potential is low [1].

Conclusion

Equations 1–3 indicate that the nature and extent of mutual electronic interactions between the metal atom and the oxalate group have a decisive influence on the mechanism of oxalate decompositon. Although the influence of other factors typical of topochemical processes on oxalate decomposition can not be discounted on the basis of Eq. 3, the complementary nature of quantitative relationships 1–3 suggests that the metal atom – oxalate bond is most decisive.

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ZUSAMMENFASSUNG — Ein Mechanismus der thermischen Zersetzung ionischer Oxalate wurde auf der Grundlage von drei quantitativen Zusammenhängen vorgeschlagen, welche die Mengen r_c/r_i (Verhältnis des Paulingschen kovalenten Radius und des Kationenradius des Metallatoms in Hexakoordination) und ΣI_i (die Summe der Ionisierungspotentiale des Metallatoms in kJ Mol^{-1}) mit der anfänglichen Zersetzungstemperatur (T_d) (Gleichung 1), der durchschnittlichen Entfernung der C—C Bindungen ($\bar{d}$) (Gleichung 2) und der Aktivierungsenergien der Oxalatzersetzung (E_a) (Gleichung 3) verbinden.

$$T_d = 516 - 1.400 \frac{r_c}{r_i} (\Sigma I_i)^{\frac{1}{2}} \qquad (1)$$

$$\bar{d} = 1.527 + 5.553 \times 10^{-6} \left(122 - \frac{r_c}{r_i} (\Sigma I_i)^{\frac{1}{2}}\right)^2 \qquad (2)$$

$$E_a = 127 + 1.4853 \times 10^{-6} \left(\left(\frac{r_c}{r_i}\right)^2 \Sigma I_i - 9800\right)^2 \qquad (3)$$

Aufgrund ihrer Ergebnisse ist der Verfasser der Ansicht, daß bei der thermischen Zersetzung von ionischen Oxalaten ein solcher Mechanismus verläuft bei welchem die C—O Bindung als erste aufgerissen wird. Sie vermuten auf Basis der angegebenen Gleichung (3), daß die sehr starke Elektroneninteraktion zwischen dem Oxalation und dem Kationen jene bedeutende Elektronenumgestaltung die zur Bildung des Produkts führt beschränkt und derart E_a erhöht ist.

Резюме — Предложен механизм термического разложения ионных оксалатов на основе трех количественных соотношений, связывающих r_c/r_i (отношение ковалентного радиуса по Полингу к радиусу металл-катиона в шестикоординационном состоянии) и ΣI_i (сумма ионизационных потенциалов атома металла, выраженная в кдж/моль) с начальной температурой T_d разложения оксалата (уравн. 1), со средним расстоянием связи С—С ($\bar{d}$) (уравн. 2/и энергией активации E_a реакции разложения оксалата (уравн. 3)

$$T_d = 516 - 1.4006 \frac{r_c}{r_i} (\Sigma I_i)^{\frac{1}{2}} \qquad (1)$$

$$\bar{d} = 1.527 + 5.553 \times 10^{-6} \left(122 - \frac{r_c}{r_i} (\Sigma I_i)^{\frac{1}{2}}\right)^2 \qquad (2)$$

$$E_a = 127 + 1.4853 \times 10^{-6} \left(\left(\frac{r_c}{r_i}\right)^2 \Sigma I_i - 9800\right)^2 \qquad (3)$$

Предположено, что термическое разложение ионных оксалатов протекает по механизму, где сначала происходит разрыв С—О связи. На основании уравнения 3 выдвинуто дальнейшее предположение, что совместное сильное электронное взаимодействие между оксалат-ионом и катионом металла существенным образом ограничивает электронную перегруппировку, приводящую к продуктам реакции, вследствие чего увеличивается E_a.