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THE THERMAL DECOMPOSITION TEMPERATURES OF IONIC METAL OXALATES

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Previous investigations linking the thermal decomposition properties of metal oxalates to the nature of the bonding have been successful only in establishing qualitative relationships. A quantitative relation is now revealed permitting prediction of the thermal decomposition temperatures T_d (°C) of metal oxalates:

$$T_d = 516 - 1.4006\, r_c/r_i \sqrt{\Sigma I}$$

where r_c/r_i is the ratio of the Pauling covalent radius and the ionic radius of the metal atom in hexacoordination, and ΣI_i is the sum of the ionization potentials of the metal atom in kJ mol^{-1}.

The thermal decomposition of metal oxalates has been the subject of numerous investigations [1–7]. The most important applications of the thermal decomposition reaction are in the fabrication of surface-active metal oxides for use in catalysis [8, 9] and in the preparation of well-defined double or multicomponent oxides which show interesting optical and electrical properties [10–12].

As regards the general trend of the thermal decomposition temperatures, the available data show a decrease of the dissociation temperature with increasing electronic interaction between the metal and oxalate ions. Therefore, the oxalates of the *d* elements display lower thermal decomposition temperatures than the oxalates of *s* and *p* metal ions of the same charge. The higher the charge on the metal ion, the tighter the binding of the metal and carboxylate groups, which increases the mutual electronic interactions.

Accordingly, the highest thermal decomposition temperature will be observed for the largest cations of the smallest charge. This generalization permits prediction of the trends of the thermal decomposition temperature, based on the position of the metallic element in the periodic table. From these considerations, the thermal decomposition temperature T_d (°C) of ionic oxalates where the metal M = alkali, alkaline earth and rare earth is found to be best defined by the relation;

$$T_d = 516 - 1.4006\, r_c/r_i \sqrt{\Sigma I_i} \tag{1}$$

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where r_c is the Pauling covalent radius of the metal, r_i is its ionic radius in hexacoordination, and ΣI_i is the sum of the ionization potentials in kJ · mol^{-1}.

Experimental

The preparation of metal oxalates from analytical grade metal oxides, hydroxides and chlorides was by methods of homogeneous precipitation employing diethyl oxalate, followed by recrystallization of the precipitates from aqueous solutions. The compositions of the metal oxalates and their hydrates obtained by air-drying of the products were established by standard methods of chemical analysis.

Results and discussion

The thermal decomposition studies in air were performed on a Linseis equipment for simultaneous TG (L81) and DTA (L62), using well-grown crystals of approximately 75 μm obtained by sieving (200 mesh). The quantities used (20–30 mg) were packed in a platinum crucible, while the reference (α-Al_2O_3) was placed in a crucible of identical dimensions. The temperature was measured with a Pt–Pt/Rh thermocouple and the heating rate 5°/minute was employed throughout.

The onset thermal decomposition temperatures obtained (Table 1) are in generally good agreement with the most recent literature values. The TG curves are similar to those from recent investigations [2, 3, 7] and therefore will not be reproduced here.

A plot of T_d against $r_c/r_i \sqrt{\Sigma I_i}$ (Fig. 1) is linear, in agreement with Eq. (1), and discrepancies occur where the oxalate decomposition is known to follow oxidation of the metal cation. For the oxalate of trivalent cerium, the oxidation of cerium has been suggested to occur prior to oxalate decomposition [13]. Con-

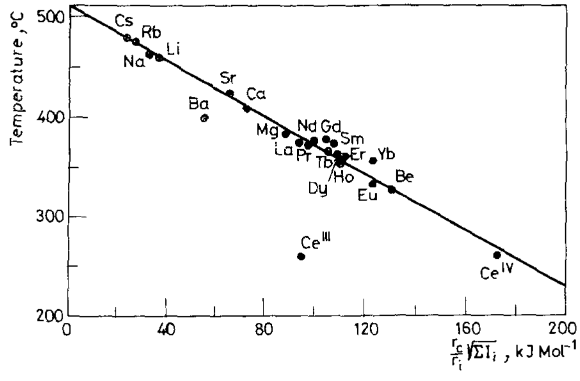

Fig. 1. Onset decomposition temperatures of metal oxalates *vs.* the ratio $\frac{r_c}{r_i}\sqrt{\Sigma I_i}$

Table 1

Onset thermal decomposition temperature of alkali metal oxalates, $M_2C_2O_4$, alkaline earth metal oxalates, MC_2O_4, and rare earth metal oxalates, $Ln_2(C_2O_4)_3$

Metal oxalate	Onset decomposition temperature, °C
$M_2C_2O_4$	
M = Li	460
Na	460–465
Rb	475
Cs	475–480
MC_2O_4	
M = Be	325–330
Mg	380–385
Ca	405–410
Sr	420–425
Ba	395–400
$Ln_2(C_2O_4)_3$	
Ln = La	375
Ce	260–265
Pr	370–375
Nd	370–375
Sm	370–375
Eu	330–335
Gd	375
Tb	365–370
Dy	360–365
Ho	350–355
Er	360–365
Yb	355–360

firmation is obtained from our studies if the ionic radius of Ce^{4+} and the respective sum of the ionization potentials are assumed, in which case the data points for $Ce_2(C_2O_4)_3$ lie on a straight line.

Conclusions

The nature of Eq. (1) suggests that the correlation of the charge-radius ratios with the thermal decomposition temperature can yield only qualitative relationships. Strictly, Eq. (1) should hold for the radius of the metal ions effective in the respective solid oxalate compound. The ionic radii used are based on experimental averages obtained from structure determinations on many compounds for each metal ion (Table 2) [14]. The deviations of these values from the effective radii of the cations in the oxalates, however, is insignificant in the present study.

Table 2

The radii, ionization potentials and values of the ratio $\frac{r_c}{r_i}(\Sigma I_i)^{1/2}$

Metal	Covalent radius r_c, Å	Ionic radius, r_i, Å	Sum of ionization potentials, kJ Mol$_{-1}$	$\frac{r_c}{r_i}(\Sigma I_i)^{1/2}$ (kJ·mol^{-1})$^{1/2}$
Li	1.225	0.74	526	37.961
Na	1.572	1.02	502	34.525
K	2.025	1.38	425	30.249
Rb	2.160	1.49	409	29.326
Cs	2.350	1.70	382	27.019
Be	0.889	0.35*	2669	131.221
Mg	1.364	0.72	2201	88.876
Ca	1.736	1.00	1748	72.581
Sr	1.914	1.16	1627	66.558
Ba	1.981	1.36	1481	56.054
La	1.690	1.061	3468	93.803
Ce(III)	1.646	1.034	3542	94.742
Ce(IV)	1.646	0.80	7091	173.257
Pr	1.648	1.031	3645	98.219
Nd	1.642	0.995	3668	99.960
Sm	1.660	0.964	3910	107.662
Eu(III)	1.850	0.950	4048	123.899
Gd	1.614	0.938	3756	105.461
Tb	1.592	0.923	3801	106.348
Dy	1.589	0.908	3920	109.572
Ho	1.580	0.894	3960	111.216
Er	1.569	0.881	3933	111.535
Yb	1.699	0.858	4231	128.803

* The cation radius of Be^{2+} in CN6 was not given [14] thus the Ahrens ionic radius in CN6 was used. The two generally show close agreement.

The covalent Pauling radii [15] are those which have been used to establish the electronegativities of the elements according to Allred–Rochow [16]. The significance of the present findings is confirmed by the correlation of the activation energies E_a and the quantities r_c/r_i and ΣI_i which will be described in a separate communication [17].

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Résumé — Les études antérieures qui reliaient les caractéristiques de la décomposition thermique des oxalates métalliques à la nature de la liaison sont restées limitées à des relations qualitatives. Une relation quantitative qui permet de prédire les températures de décomposition thermique T_d(°C) des oxalates de métaux est présentée ici:

$$T_d = 516 - 1.4006\, r_c/r_i \sqrt{\Sigma I_i}$$

où r_c/r_i est le rapport du rayon covalent de Pauling au rayon ionique de l'atome métallique hexacoordonné et ΣI_i la somme des potentiels d'ionisation de l'atome de métal en kJ·mol^{-1}.

Zusammenfassung — Frühere Untersuchungen über Beziehungen der Eigenschaften thermischer Zersetzung von Metalloxalaten in Bezug auf Bindungseigenschaften, waren nur hinsichtlich der Feststellung qualitativer Zusammenhänge erfolgreich. Es wurde ein quantitativer Zuhammenhang gefunden, welcher die Voraussage der thermischen Zersetzungstemperaturen T_d (°C) der Metalloxalate gestattet:

$$T_d = 516 - 1.4006\, r_c/r_i \sqrt{\Sigma I_i}$$

wobei r_c/r_i das Verhältnis der Pauling'schen kovalenten Radiusen und des Ionenradius des Metallatoms in sechsfacher Koordination ist und ΣI_i die Summe des Ionisierungspotentials des Metallatoms in kJ·mol^{-1}.

Резюме — Предыдущие исследования, касающиеся зависимости термического разложения оксалатов металлов от природы связи, установили только качественные соотношения. Теперь же выведено количественно уравнение, позволяющее устанавливать температуры термического разложения T_d (°C) оксалатов металлов:

$$T_d = 516 - 1.4006\, r_c/r_i \sqrt{\Sigma I_i}$$

где r_c/r_i — отношение ковалентного радиуса по Полингу и ионнорадиуса атома металла в шестикратной координации, а ΣI_i — сумма ионизационных потенциалов атома металла, выраженных в кдж·моль$^{-1}$.