

KINETICS OF THE THERMAL DECOMPOSITIONS OF MC_2O_4 TO MCO_3 (M = Ca, Sr AND Ba)

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The kinetics of the thermal decompositions of CaC_2O_4 , SrC_2O_4 and BaC_2O_4 to their carbonates were studied by thermogravimetry at constant and at linearly increasing temperatures. Isothermally, the three oxalates decompose according to $A_{1.43}$, $R_{1.54}$ and R_1 laws, respectively. Dynamically, the decompositions of the first two oxalates proceed in a similar way as under the isothermal conditions, whereas BaC_2O_4 decomposes according to a different law.

Kinetic compensation laws were established for the decomposition of CaC_2O_4 and SrC_2O_4 under both isothermal and non-isothermal conditions. Such a compensation law is considered to result if "correct" kinetic model functions $F(\alpha)$ are used when the isothermal and non-isothermal decompositions are regulated by the same $F(\alpha)$.

The kinetics of thermal decompositions of metal oxalates have been reported by many workers. The published activation energies, E , differ considerably and the significance of the value of E is still dubious. To understand the decomposition kinetics of solids, it is important to examine the processes under both isothermal and non-isothermal conditions. In addition, various kinetic model functions should be examined in the mathematical analyses [1].

Here the decomposition kinetics of CaC_2O_4 , SrC_2O_4 and BaC_2O_4 are investigated. These oxalates decompose to their carbonates and carbon monoxide [2]. In the present paper, the kinetics of decomposition of these oxalates to their carbonates are discussed only on the basis of our own data, in so far as a comparison with those reported by other workers does not seem to be of much significance. The "real" establishment of the kinetic compensation law and its significance are discussed to review the kinetics assessed conventionally.

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Experimental

The three metal oxalate hydrates were prepared through the double decompositions of $(NH_4)_2C_2O_4$ and the metal chlorides in dilute aqueous solutions. The precipitates were dried in air and sieved to a fraction of 100–170 mesh after grinding with a pestle in a mortar. The hydrated oxalates were characterized by means of IR spectroscopy and thermogravimetry (TG). The samples were obtained by dehydrating ca. 10 mg of each hydrated oxalate in a platinum crucible 5 mm in diameter and 2.5 mm in height on a Rigaku Thermoflex TG–DSC 8085 EI system in nitrogen with a flow rate of 30 ml min^{-1} . Successively, each sample was decomposed to the carbonate and carbon monoxide at various rates. Isothermal mass-change traces at different temperatures were recorded under identical conditions with dynamic runs. The kinetic analyses were made in the decomposition range of 0.1–0.9 throughout.

Results and discussion

Isothermal analysis

Figure 1 shows typical isothermal mass-change traces for the decompositions of the metal oxalates to their carbonates. We can use the following equation for analysis of the isothermal decomposition of solids:

$$F(\alpha) = kt \quad (1)$$

where $F(\alpha)$ is a function depending on the mechanism of decomposition, α is the fraction decomposed at time t , and k is the rate constant. In this study we examined

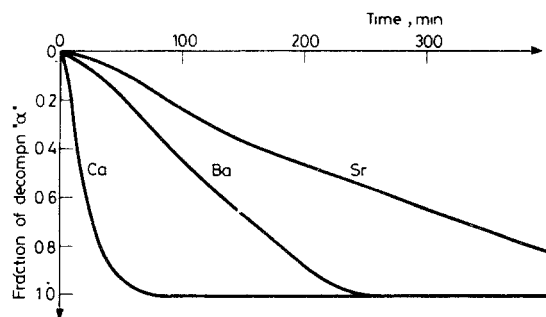


Fig. 1 Typical mass-change traces for the isothermal decompositions of MC_2O_4 into MCO_3 . At 417.4, 417.9 and 417.4 °C for $M = Ca, Ba,$ and Sr , respectively

Table 1 Appropriate $F(\alpha)$ and the kinetic parameters for the isothermal decomposition of MC_2O_4 into MCO_3

M	Temp., °C	$F(\alpha)$	E , kJ mol ⁻¹	log A , s ⁻¹	$-\gamma$	$k \times 10^{4*}$, s ⁻¹
Ca	405–424	$A_{1.43}$	180 ± 5.0	10.5 ± 0.3	0.9917	8.3548
Sr	418–437	$R_{1.54}$	270 ± 6.7	15.8 ± 0.5	0.9971	0.59941
Ba	393–421	R_1	181 ± 5.0	9.47 ± 0.44	0.9815	0.74946

* Value at 420 °C.

twelve models of $F(\alpha)$ as listed elsewhere [3]. The most appropriate $F(\alpha)$ was estimated by plotting various $F(\alpha)$ against t .

Table 1 lists the $F(\alpha)$ which gave the highest correlation coefficients γ of the linear regression analysis, together with the activation energy E and frequency factor A derived from the Arrhenius plots. The $A_{1.43}$ law for CaC_2O_4 may result from a combination of the A_1 and A_2 laws, or it may correspond to an $A_{1.5}$ law [4]. The Avrami–Erofeyev law for CaC_2O_4 suggests that the breaking of the bond in the oxalate ion is not the rate-determining step. On the other hand, the decompositions of SrC_2O_4 and BaC_2O_4 are probably regulated by the chemical reaction in the phase boundaries. The $R_{1.54}$ law for SrC_2O_4 implies a combination of the R_1 and R_2 laws.

The A values for the three oxalates are so different that the k values are more appropriate for comparing the kinetics of the decompositions of these oxalates rather than the apparent activation energy E . We see from the k values listed in Table 1 that CaC_2O_4 decomposes much faster than the other two oxalates, which means that CaC_2O_4 is much more labile kinetically.

Dynamic analysis

Figure 2 shows typical traces for the thermal decompositions of the metal oxalates to their carbonates. Table 2 lists the decomposition temperatures for the

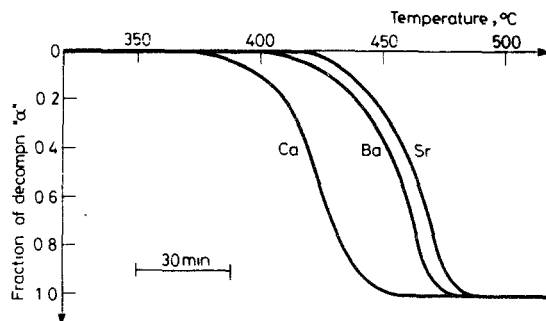
**Fig. 2** Typical TG traces for the thermal decompositions of MC_2O_4 into MCO_3

Table 2 Decomposition temperatures and standard enthalpy changes ΔH° for the thermal decomposition of MC_2O_4 into MCO_3

M	Heating rate, $K\ min^{-1}$	Temp., $^\circ C^{*1}$			ΔH° , $kJ\ mol^{-1*2}$
		T_i	$T_{0.5}$	T_f	
Ca	1.27 ± 0.09	363.5 ± 4.4	426.5 ± 1.0	455.0 ± 0.7	43.1
Sr	1.27 ± 0.01	420.3 ± 3.9	464.7 ± 0.6	485.7 ± 0.6	40.1
Ba	1.28 ± 0.01	400.8 ± 2.4	457.8 ± 1.0	478.2 ± 1.4	41.8

*¹ T_i , $T_{0.5}$ and T_f refer to the inception-, half decomposed- and final temperatures estimated from TG, respectively.

*² Calculated from standard enthalpy of formation at 25 $^\circ C$.

Table 3 Kinetic parameters derived for the dynamic decomposition of MC_2O_4 into MCO_3 using the modified Coats and Redfern's method

M	$F(\alpha)^{*1}$	E , $kJ\ mol^{-1}$	$\log A$, s^{-1}	$-\gamma^{*2}$	$k \times 10^4$, s^{-1*3}
Ca	$A_{1.43}$	258 ± 2	16.2 ± 0.2	0.9976	10.897
Sr	$R_{1.54}$	231 ± 1	13.0 ± 0.1	0.9985	0.76213
Ba	R_1	218 ± 1	12.3 ± 0.1	0.9994	1.2876

*¹ The $F(\alpha)$ determined isothermally.

*² Correlation coefficient for the linear regression analysis of the Coats and Redfern's plot.

*³ Value at 430 $^\circ C$.

three oxalates, assessed from TG, together with the corresponding enthalpy changes ΔH . Table 3 presents the kinetic parameters derived for the dynamic decompositions of the metal oxalates using a modified Coats and Redfern method [5] in terms of the same $F(\alpha)$ as those for the isothermal decompositions.

It appears rather meaningless to compare the Arrhenius parameters derived dynamically for these metal oxalates, due to the deviation of the values of A . This is also the case for a comparison of the Arrhenius parameters derived dynamically with those obtained isothermally, because of the compensation relation. It is much more informative to discuss the results on the basis of the rate constant k at a given temperature. The trend in k determined dynamically is comparable with that derived isothermally, as can be seen from Tables 2 and 3. The thermal stabilities of the three metal oxalates can be correlated with the k values listed in Table 3. It is unlikely here that the thermal stabilities of the oxalates are explained by thermodynamics only [6].

Kinetic compensation effects

Kinetic compensation laws [7] were established for the thermal decompositions of the three metal oxalates over several runs at different heating rates. Figure 3 shows the compensation plots obtained, in terms of $F(\alpha)$ estimated isothermally, for the non-isothermal decompositions of these oxalates. Table 4 lists the compensation parameters a and b , together with the correlation coefficient γ of the linear regression analysis, for the compensation equation:

$$\log A = a + bE \quad (2)$$

It is interesting that this law can be used to review the $F(\alpha)$ estimated for the decompositions of the present oxalates. Table 5 lists the Arrhenius parameters and compensation constant in terms of twelve $F(\alpha)$ for the thermal decomposition of CaC_2O_4 to $CaCO_3$, as an example, together with the values of k derived isothermally and from the compensation laws using the Arrhenius equation. It is

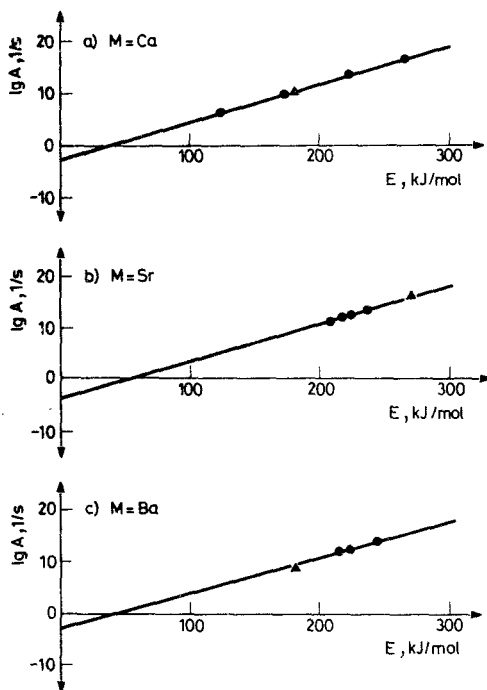


Fig. 3 Compensation plots for the non-isothermal decompositions of MC_2O_4 into MCO_3 at various heating rates in terms of the equation; $\log A = a + bE$. At heating rates of 1.14; 2.33; 5.65; 11.10 deg min^{-1} for $M = Ca$, 0.62; 1.28; 2.52; 5.16 deg min^{-1} for $M = Sr$, and 0.61; 1.30; 2.58 deg min^{-1} for $M = Ba$. \bullet and \blacktriangle are the points according to dynamic and isothermal runs, respectively

Table 4 Kinetic compensation parameters for the thermal decomposition of MC_2O_4 into MCO_3 at different heating rates

M	$F(\alpha)$	Compensation parameter* ¹		γ * ²
		$-a, \text{s}^{-1}$	$b, \text{mol kJ}^{-1} \text{s}^{-1}$	
Ca	$A_{1.43}$	2.61215	0.0728678	1.0000
Sr	$R_{1.54}$	3.72974	0.0725098	0.9919
Ba	R_1	2.98229	0.0703467	0.9998

*¹ For the equation, $\log A = a + bE$.

*² Correlation coefficient for the linear regression analysis of $\log A - E$ plot.

noted here that the $A_{1.43}$ law assumed for the non-isothermal decomposition yields the highest value of γ , which might imply that the law assumed is appropriate. At the same time, kinetic compensation effects seem to result superficially for the phase boundary and diffusion-controlled laws, if we draw conclusions on the basis of the correlation coefficient γ or the linearity of the linear regression analysis, as many workers have done so far. We believe that it is important to examine the data for various $F(\alpha)$ and then to single out the $F(\alpha)$ which gives the highest value of γ to find the "true" kinetic compensation law. We also see that in the case of the $A_{1.43}$ law the k value derived isothermally is comparable with that from the compensation law in terms of $\log A = 10.4791 \text{ s}^{-1}$ derived from the Arrhenius plot, which in turn implies that the non-isothermal decomposition is regulated by the same kinetic model as that for the isothermal one. We note that the correspondence between the k values derived isothermally and from the compensation law is similarly not bad for the R_1 law. It is likely, however, that this analogy is rather accidental, since the linearity of the $F(\alpha)$ vs t plot in terms of the R_1 law was not so good in comparison with the $A_{1.43}$ law.

With regard to the decomposition of SrC_2O_4 , the k value estimated isothermally in terms of the $R_{1.54}$ law was most comparable with that from the compensation law. In addition, the correlation coefficient γ for the linear regression analysis of the compensation plot was highest for the R_2 law. These results tend to support the $R_{1.54}$ law estimated from the $F(\alpha)$ vs t plots.

As concerns the decomposition of BaC_2O_4 , the k value estimated isothermally in terms of the R_1 law was not so comparable with that from the compensation law, but the A_1 and R_2 laws gave a fairly good correspondence. The correlation coefficient γ for the linear regression analysis of the compensation plot was highest for the R_2 law. This result does not imply that the R_2 or A_1 law regulates the isothermal decomposition, since the value of γ for the linear regression analysis of

Table 5 Kinetic parameters derived isothermally, compensation constants for the non-isothermal decomposition, and comparison of the rate constants obtained isothermally with those from the compensation law in terms of various $F(\alpha)$ for the decomposition of CaC_2O_4 into CaCO_3

$F(\alpha)$	Isothermal analysis				Compensation constant*2			Rate constant, s^{-1} *3	
	E , kJ mol^{-1}	$\lg A$, s^{-1}	$-\gamma$ *1	$-\alpha$, s^{-1}	$b \times 10^3$, $\text{mol kJ}^{-1} \text{s}^{-1}$	γ *1	Isothermally	From compensation law	
D ₁	179.796	10.1849	0.9914	5.24022	7.81016	0.9988	3.47355×10^{-4}	1.57479×10^{-5}	
D ₂	179.834	10.1251	0.9876	5.87053	7.85192	0.9989	3.00670×10^{-4}	4.63182×10^{-6}	
D ₃	182.590	9.93422	0.9883	6.88355	7.88373	0.9989	1.19692×10^{-4}	5.57029×10^{-7}	
D ₄	180.780	9.63001	0.9880	6.79441	7.89416	0.9989	8.15101×10^{-5}	6.93721×10^{-7}	
R ₁	174.733	9.81673	0.9871	3.21280	7.40564	0.9997	3.60428×10^{-4}	2.91860×10^{-4}	
R ₂	178.959	10.0151	0.9916	3.77023	7.58804	0.9998	2.71951×10^{-4}	1.69287×10^{-4}	
R ₃	179.847	9.97622	0.9917	3.84369	7.55283	0.9996	2.12923×10^{-4}	1.23234×10^{-4}	
A ₁	179.837	10.6140	0.9878	3.57700	7.61970	0.9992	9.26323×10^{-4}	3.02545×10^{-4}	
A _{1,*3}	179.948	10.4791	0.9917	2.61215	7.28678	1.0000	6.65946×10^{-4}	7.00617×10^{-4}	
A ₂	176.749	10.1189	0.9877	-5.09322	2.65250	0.3966	5.08160×10^{-4}	5.50401×10^{-5}	
A ₃	175.638	9.88177	0.9874	-3.64415	1.20935	0.1676	3.57421×10^{-4}	5.50437×10^{-30}	
A ₄	175.103	9.72862	0.9873	1.11539	4.42350	0.9460	2.75823×10^{-4}	1.33456×10^{-9}	

*1 Correlation coefficient of the linear regression analysis.

*2 For the non-isothermal runs at heating rates of 1.14, 2.32, 5.65, and 11.10 K min^{-1} .

*3 Value at 415 °C.

the $F(\alpha)$ vs. t plot in terms of the R_2 or A_1 law was not high, but that in terms of the R_1 law was highest.

The above discrepancy that the k values are different for the decomposition of CaC_2O_4 may be explained as follows: (1) The rate law for the dynamic decomposition of this oxalate is different from that for the isothermal decomposition. (2) The kinetic parameters derived from the Coats and Redfern method are ambiguous, because the highest value of γ for the linear regression analysis of the Coats and Redfern plot resulted not from the R_1 , but from the D_4 law. The D_4 law is also probable in view of the fact that the solid product becomes coagulated, probably due to sintering during the dynamic decomposition.

Conclusion

“True” kinetic compensation laws were established for the decomposition of CaC_2O_4 and SrC_2O_4 under isothermal and non-isothermal conditions, using $A_{1.43}$ and $R_{1.54}$ kinetic models, respectively. This suggests that these laws estimated from a conventional isothermal analysis are also appropriate to describe the corresponding non-isothermal decompositions.

On the other hand, only a superficial (or false) kinetic compensation law resulted for the thermal decomposition of BaC_2O_4 , which implies that the dynamic decomposition proceeds according to a different law from the isothermal one, or that the present dynamic analysis itself is not pertinent to the decomposition.

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Zusammenfassung — Die Kinetik der thermischen Zersetzung von CaC_2O_4 , SrC_2O_4 und BaC_2O_4 zu den entsprechenden Carbonaten wurde durch Thermogravimetrie bei konstanter und linear ansteigender Temperatur untersucht. Isotherm werden die drei Oxalate entsprechend $A_{1.43}$, $R_{1.54}$ bzw. R_1 zersetzt. Dynamisch verläuft die Zersetzung der ersten zwei Oxalate auf ähnlichem Wege, während BaC_2O_4 nach einem davon verschiedenem Gesetz abgebaut wird. Kinetische Kompensationsgesetze wurden sowohl unter isothermen als auch unter nicht-isothermen Bedingungen für die Zersetzung von

CaC_2O_4 und SrC_2O_4 ermittelt. Ein solches Kompensationsgesetz wird als Ergebnis eines solchen Vorgehens angesehen, bei dem „richtige“ kinetische Modellfunktionen $F(\alpha)$ benutzt werden, wenn die nicht-isothermen Zersetzungen durch die gleichen $F(\alpha)$ bestimmt sind.

Резюме — Методом ТГ при постоянной и линейно-увеличивающейся температуре изучена кинетика термического разложения оксалатов кальция, стронция и бария. При изотермическом нагреве три оксалата разлагаются, соответственно, по законам $A_{1,43}$, $R_{1,54}$ и R_1 . При динамическом нагреве разложение первых двух оксалатов протекает аналогично изотермическому, тогда как разложение оксалата бария протекает по другому закону. Кинетические компенсационные законы разложения оксалатов кальция и стронция установлены как в изотермических, так и неизотермических условиях. Такой компенсационный закон получается при использовании функций $F(\alpha)$ «корректной» кинетической модели в том случае, если изотермическое и неизотермическое разложение определяется той же самой функцией $F(\alpha)$.