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SIGNIFICANCE OF KINETIC COMPENSATION EFFECT IN THE THERMAL DECOMPOSITION OF A SOLID

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ABSTRACT

A very high correlation in the logA-E plot was obtained for the non-isothermal dehydration of $CaC_2O_4 \cdot H_2O$ at various heating rates using the most appropriate function F(α), $A_{1.9}$, estimated from isothermal analysis. Selection of the most appropriate kinetic model function and its stability under the experimental condition examined are crucial to investigate the quantitative kinetic compensation effect.

INTRODUCTION

A large number of instances of the so-called kinetic compensation effect(KCE) in solid state decompositions have so far been reported, but many of them seem to be rather qualitative. It seems important, for the moment, to investigate the KCE quantitatively at the most fundamental level possible. In view of this, it is worth studying a very simple system, e.g., the decomposition of a given solid under different experimental conditions such as the decomposition at different heating rates[1,2], which seems useful for a better understanding of the KCE as well as of kinetics of solid state decompositions in general[3-7].

We reported in previous papers that, for a given solid, kinetics of the isothermal decomposition are correlated quantitatively with those of the non-isothermal decomposition at different heating rates, in terms of the KCE[1,8,9]. That is, on plotting the apparent activation energies, E, against logarithm of the preexponential factors, A, the point given isothermally is in alignment with those derived non-isothermally in terms of the same kinetic model function. In addition it was shown that the rate constant, k, derived in terms of the KCE in the non-isothermal decomposition is in good agreement with that derived isothermally. Examination of such a correlation enabled us to review the kinetic model function, F(α), and the kinetic parameters estimated conventionally. It

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was also noted that such a quantitative correlation between the kinetic parameters is possible only when a correct kinetic model function F(α) is used.

In the present paper, kinetics of the dehydration of $CaC_2O_4 \cdot H_2O$ are reinvestigated extensively in view of the quantitative KCE.

EXPERIMENTAL

Simultaneous TG-DSC measurements were carried out for the dehydration of $CaC_2O_4 \cdot H_2O$, prepared in our laboratory, in ambient air and in flowing N_2 at a rate of 80 ml min^{-1}, using a Rigaku Thermoflex TG-DSC 8085 E1 type instrument. For the dehydration in ambient air the same data as those used in a previous study[10] were reanalyzed to examine the quantitative KCE. Concerning the dehydration in flowing N_2, data which had been obtained at that time with the same sample were analyzed.

RESULTS AND DISCUSSION

It was suggested earlier that kinetics of both isothermal and non-isothermal dehydrations of $CaC_2O_4 \cdot H_2O$ in ambient air are regulated by an Avrami-Erofeyev law Am with m=2[10]. This was supported by manifestation of the quantitative KCE in the dehydrations at different heating rates of 0.55, 1.16, 2.36, 4.71, 9.33 and 18.94 K min^{-1} including the isothermal decompositions [9]. The compensation parameters a and b are reproduced in Table 1 which were determined in terms of the equation logA = a ± bE.

It is worth being more specific about the quantitative KCE, which can be established for the non-isothermal decomposition of a given solid at various heating rates.

TABLE 1
Compensation constants in terms of the equation, logA = a + bE, using the $A_{1.8}$ and $R_{2.0}$ functions for the thermal decomposition of $CaC_2O_4 \cdot H_2O$ in ambient air

F(α)*1	-a, s^{-1}	b, mol kJ^{-1} s^{-1}	r^{*2}	$\sigma^{*3} \times 10^2$
$A_{1.8}$	1.887±0.014	0.1088±0.0002	0.9999	3.4196
$R_{2.0}$	2.773±0.037	0.1173±0.0003	0.9998	7.2367

*1 $A_{1.8}=[-\ln(1-\alpha)]^{1/1.8}$ and $R_{2.0}=1-(1-\alpha)^{1/2.0}$.

*2 Correlation coefficient of the linear regression analysis of the logA vs. E plot.

*3 Standard deviation of the least square fitting of the plot.

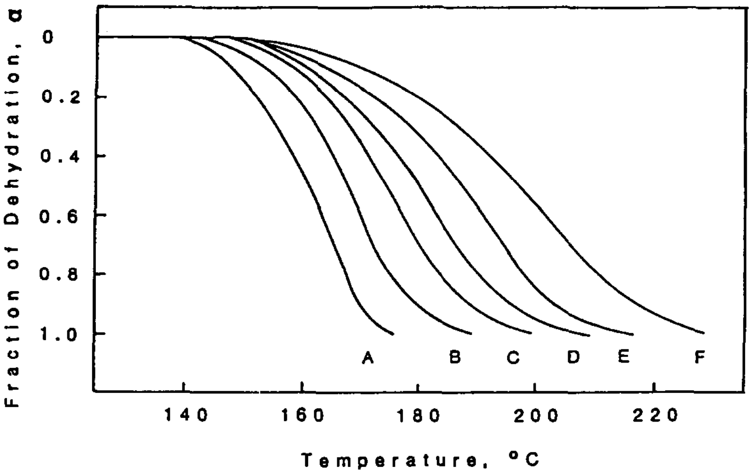

Fig. 1. TG traces of the non-isothermal dehydration of $CaC_2O_4 \cdot H_2O$ at various heating rates in ambient air. A, B, C, D, E and F refer to 0.55, 1.16, 2.36, 4.71, 9.33 and 18.94 K min^{-1}, respectively.

Figure 1 shows TG curves for the thermal dehydration of $CaC_2O_4 \cdot H_2O$ at various heating rates in ambient air. We see, as expected, that the curve shifts along the temperature coordinate to higher temperature regions with increasing heating rate, although the shape of the curves remains almost unchanged. This fact is responsible for the appearance of the quantitative KCE[11], with which we are concerned here. Table 2 shows the compensation constants a and b, together with the rate constants k derived isothermally and from the KCE using the same value of logA for each F(α).

It is noted in Table 2 that the correlation coefficients γ of the linear regression analysis of logA-E plots are unexpectedly close to unity, although the F(α)-t plots are far from linearity except A_2 and R_2 functions(see Fig.2 in Ref.10). It is likely that the linearity of the logA-E plots results partly from the plot for the dehydration in the limited range of heating rate β; $0.55<\beta<4.71$. It appears that a good compensation correlation does not always mean the quantitative KCE. It is thus important to compare the rate constants k derived isothermally and from the KCE. We see from Table 2 that the rate constant obtained isothermally is nearly equal to that from the compensation law, in terms of the $A_{1.5}$ function, which implies that the function is most appropriate for describing the present dehydration[9].

Concerning the most appropriate function, $A_{1.5}$, for the dehydration in ambient air, it is interesting to examine the influence of measuring condition

TABLE 2

Compensation constants for the non-isothermal dehydration of $CaC_2O_4 \cdot H_2O$ in ambient air at heating rates of 0.55, 1.16, 2.36 and 4.71 K min^{-1}, and comparison of the rate constants k obtained isothermally with those from the compensation law, logA = a + bE, using various $F(\alpha)$

$F(\alpha)$	Compensation constant			Rate constant, s^{-1} *	
	-a, s^{-1}	b, mol $kJ^{-1}s^{-1}$	r	Isothermally	From compensation law
D_1	4.4401	0.12556	0.99992	9.2563×10^{-4}	2.3655×10^{-4}
D_2	4.7193	0.12558	0.99990	7.4188×10^{-4}	1.3277×10^{-4}
D_3	5.9079	0.12714	0.99977	2.9846×10^{-4}	1.6151×10^{-5}
D_4	5.6279	0.12626	0.99986	2.0048×10^{-4}	2.1235×10^{-5}
R_1	2.7644	0.11809	0.99995	8.8254×10^{-4}	1.2759×10^{-3}
R_2	3.1662	0.11988	0.99997	6.9133×10^{-4}	8.2544×10^{-4}
R_3	3.1951	0.11939	0.99975	5.4231×10^{-4}	6.7343×10^{-4}
A_1	2.8458	0.12096	0.99980	2.3221×10^{-3}	2.3743×10^{-3}
$A_{1.9}$	1.9581	0.10937	0.99997	1.3250×10^{-3}	1.3059×10^{-3}
A_2	1.8857	0.10736	0.99970	1.2459×10^{-3}	8.4909×10^{-4}
A_3	1.7056	0.09397	0.99951	8.6977×10^{-4}	6.4653×10^{-8}
A_4	1.7251	0.08148	0.99876	6.7146×10^{-4}	2.2128×10^{-8}

* Calculated at 165℃, using the value of logA determined isothermally for each $F(\alpha)$.

on the compensation relationship. Table 3 shows the dependences of the heating rate range and atmosphere in the non-isothermal dehydration of $CaC_2O_4 \cdot H_2O$ on the compensation plot. Figure 2 shows the compensation plot for the non-isothermal dehydration of $CaC_2O_4 \cdot H_2O$ in the limited heating rate range. We see from Table 3 that the linearity of the compensation plot for the dehydration in the heating rate range of 0.55-4.71 K min^{-1} is a little better than that in the range of 0.55-18.94 K min^{-1}, with a little larger errors of values of a and b due to statistics. This suggests that the dehydration mechanism possibly changes at higher heating rates, 9.33 and 18.94 K min^{-1}. As can be seen from Fig.2, the points at higher heating rates deviate from the line obtained in the plot in the lower heating rate range of 0.55-4.71 K min^{-1}.

It is also seen that the values of a and b are considerably different between the dehydrations in ambient air and flowing N_2 in the comparable heating rate ranges. This implies that the mechanism regulating the dehydration is affected by the atmosphere. It is interesting that the linearity of the compensation plot for the dehydration in flowing N_2 is a little worse than that for the dehydration in ambient air(see Table 3). We assume that using an $F(\alpha)$ different from $A_{1.9}$ is responsible for the worse deviations since we used

TABLE 3

Compensation constants in terms of $A_{1.9}$ for the non-isothermal dehydration of $CaC_2O_4 \cdot H_2O$

Atmosphere	Range of heating rate, K min^{-1}	$-a$, s^{-1}	b, mol $kJ^{-1}s^{-1}$	r	$\sigma^* \times 10^2$
Ambient air	0.55-18.94	1.8163 (±0.0131)	0.10782 (±0.00017)	0.99994	2.32
Ambient air	0.55-4.71	1.9581 (±0.0210)	0.10937 (±0.00024)	0.99997	1.40
N_2 flow (80ml/min)	0.53-18.42	2.4629 (±0.0379)	0.12450 (±0.00043)	0.99967	10.2
N_2 flow (80ml/min)	0.53-4.48	2.7559 (±0.0437)	0.12716 (±0.00044)	0.99990	5.57

* Standard deviation of the least square fitting of the logA-E plot.

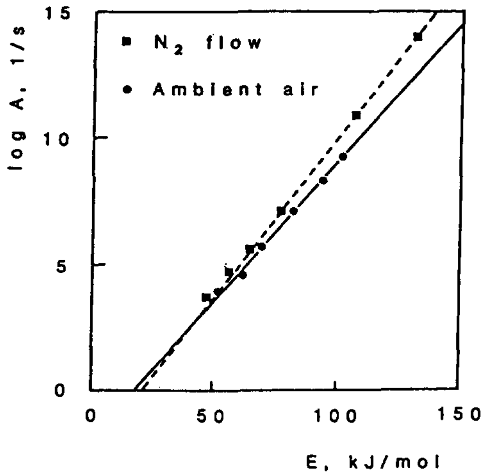

Fig. 2. Compensation plots for the non-isothermal dehydration of $CaC_2O_4 \cdot H_2O$.

$A_{1.9}$ for both the plots. If the TG curves could shift along the temperature coordinate without change in the mechanistic model, the values of a and b would be identical between the different atmospheres; all the points could be correlated by a single straight line in the compensation plot(see Fig.2).

CONCLUSION

The quantitative kinetic compensation effect(KCE) was established for the non-isothermal dehydration of $CaC_2O_4 \cdot H_2O$ in ambient air at various heating rates, in terms of a kinetic model function, $A_{1.8}$, determined isothermally. The rate constant k determined isothermally was nearly equal to that calculated in terms of the quantitative KCE at a given temperature. This fact implies that the F(α) used is appropriate for both the isothermal and non-isothermal dehydrations of $CaC_2O_4 \cdot H_2O$. On the other hand, an apparent KCE, which yields different values of a and b, resulted from the plot of logA vs. E for the dehydration in flowing N_2 at various heating rates, in terms of the same function. The above difference in the compensation correlations between the two compensation plots is caused by a possible change in the kinetic mechanism of the dehydration in an atmosphere of flowing N_2.

REFERENCES

1 H. Tanaka and N. Koga, J. Therm. Anal., 32(1987)1521.

2 A.V. Nikolaev and V.A. Logvinenko, J. Therm. Anal., 10(1976)363.

3 J. Sestak, in G. Svehla(Ed.), Comprehensive Analytical Chemistry, Vol. 12, Part D, Elsevier, Amsterdam(1984), p. 202.

4 A.K. Galwey, Thermal Analysis, Vol. 1, Proc. 7th ICTA, Kingston, 1982, Wiley Heydon, Chichester, 1982, p. 38.

5 E.P. Manche and B. Carroll, Thermochim. Acta, 31(1979)387.

6 G.G.T. Guarini and R. Spinicci, J. Chem. Soc. Dalton(1978)1484.

7 P.K. Gallagher and D.W. Johnson Jr., Thermochim. Acta, 14(1976)255

8 N. Koga and H. Tanaka, J. Therm. Anal., in press.

9 H. Tanaka and N. Koga, J. Therm. Anal., in press.

10 H. Tanaka, S. Ohshima, S. Ichiba and H. Negita, Thermochim. Acta, 48(1981)137.

11 J. Zsako, J. Therm. Anal., 9(1976)101.