Journal of Thermal Analysis, Vol. 8 (1975) 393—403

KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION PROCESSES OF CERTAIN COBALT AND TITANIUM COPRECIPITATES

M. STRĂJESCU and E. PERŢE

Institute of Chemistry, Cluj—Napoca, Romania

(Received April 23, 1974)

The kinetic parameters of the thermal decomposition reactions of certain coprecipitates were calculated by a thermogravimetric method. The significance of the results with regard to this type of coprecipitate and to the formation of the double oxides of cobalt and titanium is discussed.

The applicability of the data of thermogravimetric analysis to estimate the kinetic parameters of solid state reactions accompanied by weight changes has been investigated by several authors [1—5]. The optimum conditions of thermogravimetric analysis were established.

The kinetic study of heterogeneous reactions by thermogravimetric methods was carried out in particular for reactions of the type:

$$A(s) \rightarrow B(s) + C(g)$$

At least formally, all the reactions which take place in the thermal decompositions of the coprecipitates discussed here follow this reaction scheme. Thus, in the most complicated case, the reactions occurring during the thermal decompositions of such coprecipitates are as follows:

I — R_0, R_1 and R_2:
Coprecipitate(s) → Carbonate(s) + H_2O(g)

II — R_3:
Carbonate(s) → Double oxide 1(s) + CO_2(g)

III — R_4:
Double oxide 1(s) → Double oxide 2(s) + O_2(g)

IV — R_5:
Double oxide 2(s) → Double oxide 3(s) + O_2(g)

V — R_6:
Double oxide 3(s) → Double oxide 4(s) + O_2(g)

(By "$R_0 - R_6$" we have designated the type of the chemical reaction; by "double oxide 1—4" an oxide which results from a chemical reaction of the type $R_0 - R_6$ but is not stoichiometric.)

Depending on the composition of the coprecipitates, one or more of these reactions do not take place.

The coprecipitates were prepared by mixing solutions of $CoCl_2$, $TiCl_4$ and $(NH_4)_2CO_3$ [6]. They have the compositions designated symbolically by 0p, 11c−9c and 10p (p = precipitate and c = coprecipitate), which can be obtained from the first member of the reactions given below.

The reactions occurring for every coprecipitate, as evidenced by thermal analysis (Fig. 1), infrared absorption spectrophotometry, X-ray diffraction and chemical analysis [7, 9] are as follows:

0p $TiO_2 \cdot 1.2H_2O(s)$
$R_1 \ \downarrow$
$TiO_2 \cdot 0.5H_2O(s) + 0.7H_2O(g)$
$R_2 \ \downarrow$
$TiO_2 \cdot xH_2O(s) + (0.5 - x)H_2O(g)$
$R_0 \ \downarrow$
$TiO_2(s) + xH_2O(g)$

1c $9.3TiO_2 \cdot 8H_2O \cdot 0.5Co(OH)_2 \cdot 0.5CoCO_3(s)$
$R_1 \ \downarrow$
$9.3TiO_2 \cdot 4.5H_2O \cdot 0.5CoO \cdot 0.5CoCO_3(s) + 4H_2O(g)$
$R_2 \ \downarrow$
$9.3TiO_2 \cdot 0.5CoO \cdot 0.5CoCO_3(s) + 4.5H_2O(g)$

For other reactions insufficient data are available.

2c $4TiO_2 \cdot 2.8H_2O \cdot 0.5Co(OH)_2 \cdot 0.5CoCO_3(s)$
$R_1 \ \downarrow$
$4TiO_2 \cdot 2H_2O \cdot 0.5CoO \cdot 0.5CoCO_3(s) + 1.3H_2O(g)$
$R_2 \ \downarrow$
$4TiO_2 \cdot 0.5CoO \cdot 0.5CoCO_3(s) + 2H_2O(g)$

For other reactions insufficient data are available.

3c $2TiO_2 \cdot 1.4H_2O \cdot 0.5Co(OH)_2 \cdot 0.5CoCO_3(s)$
$R_1 \ \downarrow$
$2TiO_2 \cdot H_2O \cdot 0.5CoO \cdot 0.5CoCO_3(s) + 0.9H_2O(g)$
$R_2 \ \downarrow$
$2TiO_2 \cdot 0.5CoO \cdot 0.5CoCO_3(s) + H_2O(g)$
$R_3 \ \downarrow$
$1/3Co_3O_4 \cdot 2TiO_2(s) + 0.5CO_2(g)$
$R_4 \ \downarrow$
$CoO \cdot 2TiO_2(s) + 1/6O_2(g)$

4c $3.3TiO_2 \cdot 2.5H_2O \cdot Co(OH)_2 \cdot CoCO_3(s)$
$R_1 \ \downarrow$
$3.3TiO_2 \cdot 1.5H_2O \cdot CoO \cdot CoCO_3(s) + 2H_2O(g)$
$\downarrow$

R_2
$3.3TiO_2 \cdot CoO \cdot CoCO_3(s) + 1.5H_2O(g)$
R_3 ↓
$2/3Co_3O_4 \cdot 3.3TiO_2(s) + CO_2(g)$
R_4 ↓
$2CoO \cdot 3.3TiO_2(s) + 1/3O_2(g)$

5c $2TiO_2 \cdot 2H_2O \cdot Co(OH)_2 \cdot CoCO_3(s)$
R_1 ↓
$2TiO_2 \cdot H_2O \cdot CoO \cdot CoCO_3(s)$
R_2 ↓
$2TiO_2 \cdot CoO \cdot CoCO_3(s) + H_2O(g)$
R_3 ↓
$2/3Co_3O_4 \cdot 2TiO_2(s) + CO_2(g)$
R_4 ↓
$2(CoO \cdot TiO_2)(s) + 1/3O_2(g)$

6c $TiO_2 \cdot 1.36H_2O \cdot 0.75Co(OH)_2 \cdot 0.75CoCO_3(s)$
R_1 ↓
$TiO_2 \cdot 0.5H_2O \cdot 0.75CoO \cdot 0.75CoCO_3(s) + 1.61H_2O(g)$
R_2 ↓
$TiO_2 \cdot 0.75CoO \cdot 0.75CoCO_3(s) + CO_2(g)$
R_3 ↓
$0.5Co_3O_4 \cdot TiO_2(s) + CO_2(g)$
R_4 ↓
$1/6Co_3O_4 \cdot CoO \cdot TiO_2(s) + 1/6O_2(g)$
R_5 ↓
$1.5CoO \cdot TiO_2(s) + 1/12O_2(g)$

7c $TiO_2 \cdot 1.3H_2O \cdot 0.9Co(OH)_2 \cdot 0.9CoCO_3(s)$
R_1 ↓
$TiO_2 \cdot 0.5H_2O \cdot 0.9CoO \cdot 0.9CoCO_3(s) + 1.8H_2O(g)$
R_2 ↓
$TiO_2 \cdot 0.9CoO \cdot 0.9CoCO_3(s) + 0.5H_2O(g)$
R_3 ↓
$0.6Co_3O_4 \cdot TiO_2(s) + 0.9CO_2(g)$
R_4 ↓
$0.8/3Co_3O_4 \cdot CoO \cdot TiO_2(s) + 1.6O_2(g)$
R_5 ↓
$1.8CoO \cdot TiO_2(s) + 0.4/3O_2(g)$

8c $TiO_2 \cdot 1.6H_2O \cdot 1.6Co(OH)_2 \cdot 2.2CoCO_3(s)$
R_1 ↓
$TiO_2 \cdot 0.5H_2O \cdot 1.6CoO \cdot 2.2CoCO_3(s) + 2.7H_2O(g)$
R_2 ↓
$TiO_2 \cdot 1.6CoO \cdot 2.2CoCO_3(s) + 0.5H_2O(g)$
↓

R_3
$3.8/3Co_3O_4 \cdot TiO_2(s) + 2.2CO_2(g)$
$R_4 \quad \downarrow$
$2.8/3Co_3O_4 \cdot CoO \cdot TiO_2(s) + 1.6O_2(g)$
$R_5 \quad \downarrow$
$1.8/3Co_3O_4 \cdot 2CoO \cdot TiO_2(s) + 1.6O_2(g)$
$R_6 \quad \downarrow$
$3.8CoO \cdot TiO_2(s) + 0.3O_2(g)$

9c $TiO_2 \cdot 3H_2O \cdot 2.5Co(OH)_2 \cdot 4CoCO_3(s)$
$R_1 \quad \downarrow$
$TiO_2 \cdot 0.5H_2O \cdot 2.5CoO \cdot 4CoCO_3(s) + 5H_2O(g)$
$R_2 \quad \downarrow$
$TiO_2 \cdot 2.5CoO \cdot 4CoCO_3(s) + 0.5H_2O(g)$
$R_3 \quad \downarrow$
$6.5Co_3O_4 \cdot TiO_2(s) + CO_2(g)$
$R_4 \quad \downarrow$
$5.5/3Co_3O_4 \cdot CoO \cdot TiO_2(s) + 1/6O_2(g)$
$R_5 \quad \downarrow$
$4.5/3Co_3O_4 \cdot 2CoO \cdot TiO_2(s) + 1.6O_2(g)$
$R_6 \quad \downarrow$
$6.5CoO \cdot TiO_2(s) + 4.5O_2(g)$

10p $[Co(OH)_2 \cdot 2CoCO_3] \cdot 1.6H_2O(s)$
$R_1 \quad \downarrow$
$CoO \cdot 2CoCO_3(s) + H_2O(g)$
$R_3 \quad \downarrow$
$Co_3O_4(s) + 2CO_2(g)$
$R_6 \quad \downarrow$
$3CoO(s) + 1/2O_2(g)$

To find the integral kinetic equations in which the variable is the temperature instead of the time, we used diverse variants of the fundamental formulas of chemical kinetics such as:

$$\frac{dg}{dt} = k(g_0 - g)^n$$

$$k = k_0 e^{-E/RT}$$

where g is the decrease of the amount of substance A at moment t, g_0 is the initial amount of substance A, and k, k_0, E and n are, respectively, the kinetic constant, the pre-exponential factor, the activation energy and the reaction order.

To calculate the kinetic parameters we used the Freeman–Carroll method [2] with several amendments made by Lukaszewski and Redfern [4]. The method starts with the introduction of the variable $X = g_0 - g$ into the relationship given above, when the following relation is obtained:

$$-\frac{\mathrm{d}X}{\mathrm{d}t} = kX^n$$

If during the reaction, the amount W_r of the volatile component which is not removed at time t or at temperature T is followed, the equation allowing estimation of the kinetic parameters is as follows:

$$\frac{\frac{E}{2.303R} \cdot \Delta \frac{1}{T}}{\Delta \log W_r} = -n + \frac{\Delta \log \frac{\mathrm{d}W}{\mathrm{d}t}}{\Delta \log W_r}$$

where Δ is a difference operator and $\frac{\mathrm{d}W}{\mathrm{d}t}$ is the rate of elimination of the volatile component.

The graphical representation of the ratio $\frac{\Delta \log \frac{\mathrm{d}W}{\mathrm{d}t}}{\Delta \log W_r}$ versus $\frac{\Delta \left(\frac{1}{T}\right)}{\Delta \log W_r}$ is expected to be a straight line; the activation energy (E) can be estimated from its slope, the reaction order (n) being given by the intercept. Otherwise, these are the only kinetic parameters that can be estimated by the Freeman – Carroll method.

It is necessary to underline that W_r can be calculated by subtracting the weight loss at time t, (W), from the weight loss at the end of the reaction (W_c):

$$W_r = W_c - W$$

The method requires the use of a thermogravimetric curve only. The thermogravimetric curves given in Fig. 1 were used.

The steps of the thermal decomposition of every precipitate and coprecipitate were determined just by following the shape or the changes of the thermogravimetric curves. The rate of the weight loss for every step in mg/min, was plotted as a function of the temperature to give the DTG curves (Fig. 2). To get higher accuracy, the thermogravimetric curves were scaled up. The incidental points that did not join the considered part of the thermogravimetric curves were not taken into consideration. The weight loss was calculated in every minute, and on the basis of the linear variation of the temperature as a function of the time the differential curves were plotted.

These curves show that the process of dehydration of the coprecipitates takes place in two steps, in accordance with the two modes in which the water is bound. In the case of hydrated titanium dioxide three dehydration steps were found, which suggests that there are different modes of bonding of the hydroxyl ions; at higher temperatures the water is held by chemisorption forces [9]. In contrast, in the case of basic cobalt carbonate, the water is lost in one step. Every other reaction which takes place during the thermal decomposition of the coprecipitates occurs in one step.

To obtain the straight lines, the values of the ratios P and Q were calculated for every step:

$$P = \frac{\Delta \log \frac{\mathrm{d}W}{\mathrm{d}t}}{\Delta \log W_r} \qquad Q = \frac{\Delta \left(\frac{1}{T}\right)}{\Delta \log W_r}$$

For the decomposition of the carbonate in the case of coprecipitate 6c (see reaction R_3 given above and Fig. 2) the values are the following:

$$-\frac{E}{2.303R} = -\frac{4.8}{0.700} = -6.875$$

$$E = 2.303 \times 1.988 \times 6.875 = 30.64 \text{ Kcal/mole}$$

$$n = 0.35$$

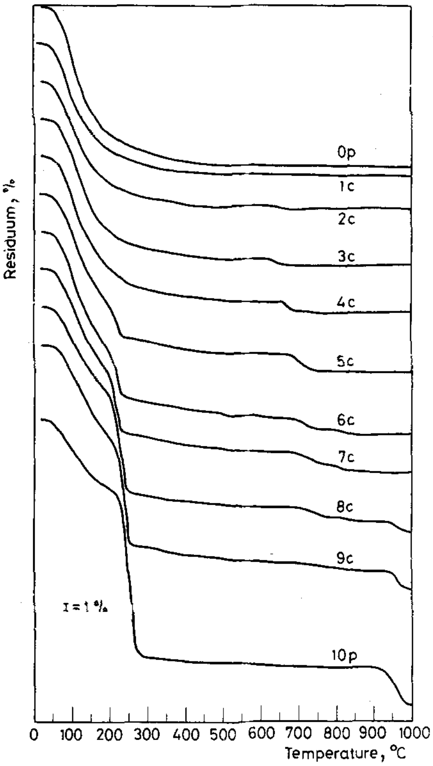

Fig. 1. TG curves of the coprecipitates (1c—9c), hydrated titanium dioxide (0p) and basic cobalt carbonate (10p). The curves have been recorded by an apparatus without automatic recording; samples size: about 1 g, in a platinum crucible

The plot of P versus Q gives a straight line if only the linear parts of the differential thermogravimetric curves are taken into account. Deviations from linearity are observed for the portions situated near the peaks, at the beginnings and the ends of the differential thermogravimetric curves, as well as for the positive values of P.

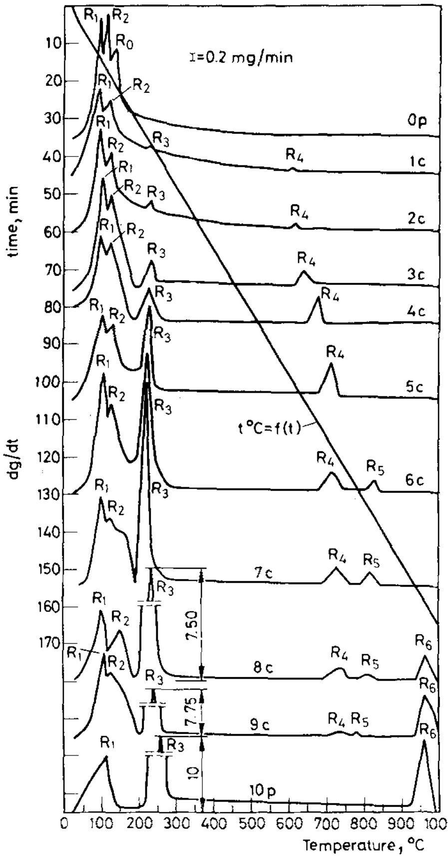

Fig. 2. DTG curves of the coprecipitates (1c—9c), hydrated titanium dioxide (0p) and the basic cobalt carbonate (10p)

In some cases the accuracy of the values E and n is not very high because of the small number of P and Q values owing to the short time of display of the reactions and because of some assumptions. For example, in the case of reactions R_3 it was considered that the oxygen for formation of Co_3O_4 results from the substance which is decomposed. The assumption is justified because in the calculations the changes of the weight are taken into account without the specification of the reactants. For this reason the stoichiometry of reactions R_3 was not considered.

Nevertheless, the values obtained for the activation energies and the reaction orders (Table 1) are similar to those given in the literature [2–4]. Moreover, they allow certain estimations to be made about the thermal decomposition processes. Comparison of the calculated values shows that the chemical forces which keep the water in the precipitates are stronger than in coprecipitates. The removal of the water in the first step (R_1) requires, in general, a higher activation energy than in the second step (R_2). This proves the chemical bonding of the water in coprecipitates. This is also supported by the higher values of the reaction order in the first case.

Table 1

The activation energies (*E*) and the reaction orders (*n*) of the thermal

Number of the sample	Step of reaction					
	R_0		R_1		R_2	
	E	*n*	*E*	*n*	*E*	*n*
0p	4.65	0.01	19.3	0.32	20.8	0.35
1c	—	—	6.99	0.05	3.07	0.02
2c	—	—	11.8	0.37	5.08	0.03
3c	—	—	15.5	0.3	5.12	0.03
4c	—	—	11.4	0.2	4.33	0.03
5c	—	—	8.6	0.3	1.87	0.004
6c	—	—	11.1	0.22	11.7	0.15
7c	—	—	12.1	0.25	1.41	0
8c	—	—	7.7	0.08	6.57	0.08
9c	—	—	9.9	0.06	2.7	0.62
10p	—	—	18.6	0.75	—	—

Except for coprecipitate 3c, the activation energies of the thermal decomposition reactions of the carbonates (R_3) rise slowly with the rise of the amount of the cobalt from one coprecipitate to another. The similar values of the reaction orders and of the activation energies, in accordance with the observations made above about the bonding of the water, are additional proofs of the assumption that in the coprecipitates the cobalt and titanium are chemically bound like a basic cobalt and titanium carbonate [6].

The decomposition reaction of Co_3O_4 with formation of cobalt metatitanate ($CoO \cdot TiO_2$), R_4, requires smaller activation energies as the amount of cobalt increases in the coprecipitate. The similar reaction orders indicate the breaking of some chemical bonds of the same energy, and in fact the same type of reaction. Because of the differences in composition, these bonds should belong to the same structural type. This leads to the conclusions that in these oxide systems, the possibility of formation of cobalt metatitanate depends mostly on the increase of the amount of cobalt from one system to another.

With regard to the decomposition of Co_3O_4 (coprecipitates 6c – 8c) with formation of cobalt orthotitanate ($2CoO \cdot TiO_2$), R_5, we meet the same situation as in the previous case (R_4), as long as the systems do not contain an amount too large of cobalt (coprecipitate 9c). In the last case, the value of the activation energy suddenly increases, whereas in the previous systems the values decreased. This fact can be accounted for by the inability of cobalt oxides to form solid solutions with cobalt titanates. When there is a small excess of cobalt oxide in a system, over the stoichiometric ratio in the orthotitanate, the first oxide cannot prevent formation of the latter. If in another system the amount of cobalt oxide is larger, Co_3O_4 preserves the crystalline lattice and higher activation energies are necessary to destroy it, and also to decompose the amount of the Co_3O_4, necessary for the formation of cobalt orthotitanate. The same fact accounts for the differences between the reaction orders of reaction R_4 and R_5 in the cases of coprecipitates 6c and 7c.

decomposition processes of the coprecipitates

R_3		R_4		R_5		R_6	
E	*n*	*E*	*n*	*E*	*n*	*E*	*n*
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
41.4	0.4	131	0.4	—	—	—	—
27.3	0.5	137	0.5	—	—	—	—
29.7	0.3	131	0.45	—	—	—	—
30.6	0.35	104	0.3	168	0.25	—	—
33.4	0.3	85.5	0.3	161	0.4	—	—
34.0	0.4	79.1	0.4	89.5	0.42	279	0.7
35.4	0.35	76.5	0.43	219	0.4	301	0.75
33.2	0.5	—	—	—	—	206	0.75

The high and similar values of the activation energies of the reaction of decomposition of the last part of the Co_3O_4 (R_6), support the finding [10] that in the double oxides, the state of the Co_3O_4 is better preserved at high temperatures than when the Co_3O_4 is alone. Vice versa, this finding is proof of the fact that in these systems double oxides were formed.

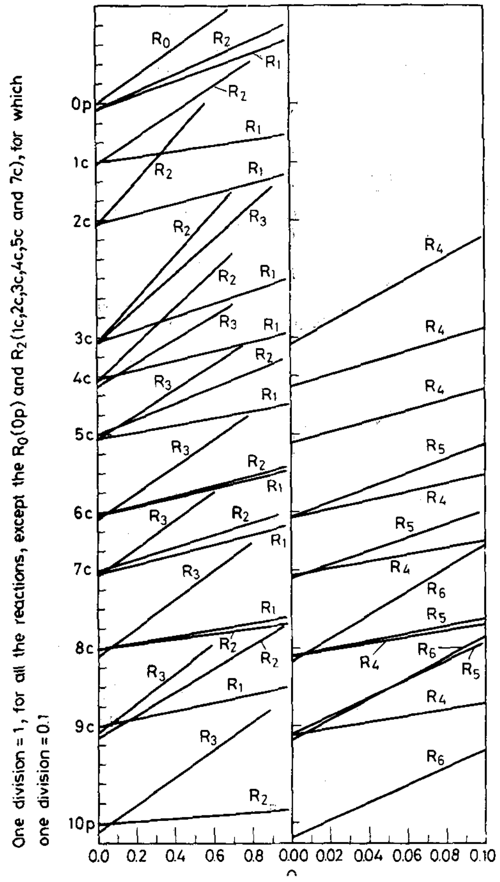

Fig. 3. Graphical representation of the kinetic equations of the thermal decomposition processes of precipitates (0p and 10p) and coprecipitates (1c—9c)

References

1. P. D. Garn, Thermoanalytical methods of investigation, Academic Press, New York, London, 1965.
2. E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
3. A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
4. G. M. Lukaszewski and J. P. Redfern, J. Chem. Soc., (1962) 4802.
5. I. G. Murgulescu and E. Segal, Studii și Cercetari Chim. Acad. R. P. R., 15 (1967) 261.
6. M. Străjescu, C. Gh. Macarovici, M. Birou and E. Perţe, Stud. Univ. Babeş-Bolyai, Chem., (1974) 32.
7. M. Străjescu, C. Gh. Macarovici and E. Perţe, Stud. Univ. Babeş-Bolyai, Chem., (1974) 38.
8. M. Străjescu and E. Perţe, J. Thermal Anal., 8 (1975) 57.
9. C. Heitner-Wirguin and A. Albu-Yaron, J. Inorg. Nucl. Chem., 28 (1966) 2379.
10. J. M. Pâris and R. A. Pâris, Bull. Soc. Chim. France, 4 (1965) 1138.

Résumé — On calcule les paramètres cinétiques des réactions de décomposition thermique de certain coprécipités et de titane. On discute la signification des résultats en relation avec ce type de coprécipités et avec la formation des oxydes doubles de cobalt et de titane.

Zusammenfassung — Die kinetischen Parameter der thermischen Zersetzungsreaktionen von einigen gemischten Niederschlägen des Kobalts und Titans wurden unter Anwendung einer thermogravimetrischen Methode berechnet. Im Hinblick auf die Art der Mitfällung und die Bildung von Kobalt und Titan Doppeloxyden wurden die Ergebnisse diskutiert.

Резюме — С помощью термогравиметрического метода были вычислены кинетические параметры реакций термического разложения соосажденных кобальта и титана. Обсуждено значение полученных результатов относительно этого типа осадков, а также образование двойных окислов кобальта и титана.