Journal of Thermal Analysis, Vol. 36 (1990) 2139-2145

DETERMINATION OF THE KINETIC PARAMETERS OF THERMAL DECOMPOSITION OF $[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$ BY KISSINGER'S METHOD

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The values of the kinetic parameters E and A were determined by Kissinger's method on the basis of the DTA, DTG and DSC curves of particular stages of the thermal decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3\cdot 4H_2O$ in air and argon atmospheres. It is shown that the use of Kissinger's method for different kinds of experimental curves (DTA, DSC, DTG) leads to close results.

Among the thermal analysis methods applied for determination of the kinetic parameters of thermal decomposition of solids, thermogravimetry is mostly used. The treatment of the TG data obtained under non-isothermal and isothermal conditions requires an a priori knowledge of the appropriate $f(\alpha)$ or $g(\alpha)$ function describing the experimental TG curves, i.e. the proper kinetic model of the dissociation process. Instead, the use of DTA or DSC measurements with the above-mentioned goal is mostly based on simplified procedures for determination of the activation energy, E (the "peak temperature methods" originally proposed by Kissinger [1, 2]). These methods do not require a search for an adequate $f(\alpha)$ or $g(\alpha)$ function which is undoubtedly an advantage.

The popular Kissinger dependence (1) has been used for the direct calculation of E from the shift in the DTA peak temperature with change of the heating rate β:

$$\ln (T_p^2/\beta) = \ln (E/R) - \ln (A) + E/RT \qquad (1)$$

where: T_p - absolute temperature (K) of the DTA peak
E - activation energy (kJ mol^{-1})
R - universal gas constant (8.314 kJ mol^{-1} deg^{-1})

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A - pre-exponential factor (min^{-1})
β - heating rate ($\mathrm{deg\ min}^{-1}$ or $\mathrm{K\ min}^{-1}$)

Kissinger initially showed [1] that his method could be used to determine E for a first-order reaction. He then extended the method to reactions of any order [2]. However, numerous shortcomings of the methods based upon Kissinger's assumption have been presented in the literature, e.g. [3-6]. The most controversial is Kissinger's assumption that the temperature of the maximum deflection in differential thermal analysis is also the temperature at which the reaction rate is a maximum [1, 2]. This assumption has been strongly criticized [3-6] and it has been argued that, even in cases where it may be approximately valid, it may lead to large errors in the kinetic parameters. Louis and Garcia-Cordovilla [5, 6] have proved that Kissinger's assumption, although not being valid for DTA, holds for DSC.

Since it is frequently assumed that the DTA signal, ΔT, is proportional to the reaction rate, $-\mathrm{d}x/\mathrm{d}t$, the possibility of using Kissinger's method for DTG curves also exists, just as for DTA or DSC. In DTG method, the reaction rate, $-\mathrm{d}x/\mathrm{d}t$ is recorded *vs.* T when the sample is heated at a linear heating rate β. The DTG peaks are slightly shifted in relation to the DTA peaks.

As shown in the article by Kirsh [7], methods of kinetic analysis which have been developed for DTG are generally not directly applicable to DTA. This is because the reaction rate, $-\mathrm{d}x/\mathrm{d}t$, is not proportional to the DTA signal, ΔT, but rather to $\Delta T + (C/K)\,\mathrm{d}(\Delta T)/\mathrm{d}t$, where C is the heat capacity of the sample and K is the heat transfer coefficient. Only when the sample is small is the error arising from the use of DTG for DTA methods (and conversely) negligible.

In spite of the above-mentioned shortcomings of Kissinger's method, the kinetic data determined with this method are in relatively good agreement with the data obtained from complementary measurements under less "non-standard" conditions (most often TG [3, 8]).

Recently, Elder discussed the general applicability of the Kissinger equation in thermal analysis [9]. On the basis of computer modelling calculations, he concluded that a modified [9] Kissinger equation is generally applicable in analyzing the thermally induced extent and rate of reaction data, yielding correct values for the kinetic parameters, E and A. However, even if the simple form of Kissinger's equation (1) is used, the resulting E values are correct. The values of the logarithmic correction term introduced by Elder [9] (the modified Kissinger equation) are relatively small, with the exception of the three-dimensional diffusion-controlled models.

The purpose of the present work was to determine the kinetic parameters *E* and *A* of the thermal decompositions of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$ by Kissinger's method on the basis of the DTA, DSC and DTG curves.

Experimental

The complex $[Co(NH_3)_6]_2(C_2O_4)_3.4H_2O$ was prepared by the literature method [10].

The quantitative analysis data are in good agreement with the chemical formula of the complex under study.

Simultaneous TG-DTG-DTA curves were recorded under non-isothermal conditions with a derivatograph C (MOM, Budapest) at 298-773 K in static air and flowing argon (4 $dm^3\ h^{-1}$) atmospheres.

The DSC curves were recorded with a UNIPAN DSC type 605 apparatus at 298-700 K in a static air atmosphere.

The measurements of the thermal decomposition of the ammine complex were performed at eight different heating rates (β varying between 20±0.5 deg min^{-1} for the derivatograph C, and between 20 and 0.2 deg min^{-1} for the microcalorimeter).

The sample weight was 10 mg, and the sieve mesh was ≤0.056 mm (specific surface 4.94 m^2g^{-1}).

Results and discussion

The thermal decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$ proceeds in three stages in both air and argon gaseous atmospheres, as proved earlier [11, 12]. The probable decomposition sequences of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$ presented in [11, 12] are as follows: Stage I (air, argon):

$$[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O \xrightarrow{endo} Co(NH_3)_5C_2O_4]_2(C_2O_4) + \\ + 2\,NH_3 + 4\,H_2O \qquad (2)$$

Stage II (air, argon):

$$3[\mathrm{Co(NH_3)_5C_2O_4}]_2(\mathrm{C_2O_4}) \xrightarrow{\text{endo}} 6\,\mathrm{CoC_2O_4} + \mathrm{N_2} + 28\,\mathrm{NH_3} + 3\,\mathrm{H_2O} + 3\,\mathrm{CO} + 3\,\mathrm{CO_2} \quad (3)$$

Stage III (air)

$$3\,\mathrm{CoC_2O_4} \xrightarrow{\text{exo}} \mathrm{Co_3O_4} + 4\,\mathrm{CO} + 2\,\mathrm{CO_2} \quad (4)$$

Stage III (argon):

$$\mathrm{CoC_2O_4} \xrightarrow{\text{endo}} \mathrm{Co_{met}} + 2\,\mathrm{CO_2} \quad (5)$$

$$\mathrm{CoC_2O_4} \xrightarrow{\text{endo}} \mathrm{CoO} + \mathrm{CO} + \mathrm{CO_2} \quad (6)$$

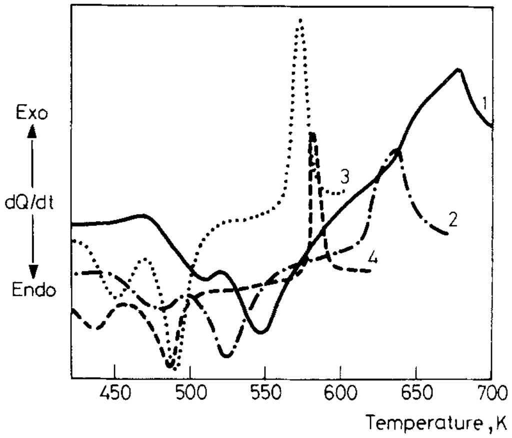

Fig. 1 DSC curves of the thermal decomposition of $[\mathrm{Co(NH_3)_6}]_2(\mathrm{C_2O_4})_3\cdot 4\mathrm{H_2O}$ in static air atmosphere. 1 - $\beta = 20$ deg min^{-1}, 2 - $\beta = 10$ deg min^{-1}, 3 - $\beta = 5$ deg min^{-1}, 4 - $\beta = 2$ deg min^{-1},

The stable solid intermediate written as $\mathrm{CoC_2O_4}$ in stage II is in fact $\mathrm{Co[Co(C_2O_4)_2]}$, as proved on the basis of far IR spectra and magnetic susceptibility measurements [13].

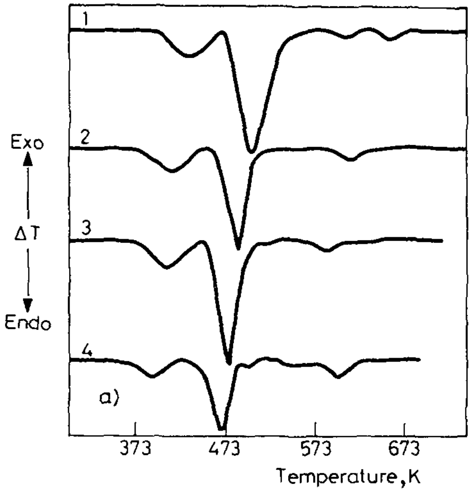

Fig. 2a DTA curves of the thermal decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$; in flowing argon atmosphere; 1 - $\beta = 20$ deg min^{-1}, 2 - $\beta = 10$ deg min^{-1}, 3 - $\beta = 5$ deg min^{-1}, 4 - $\beta = 2$ deg min^{-1},

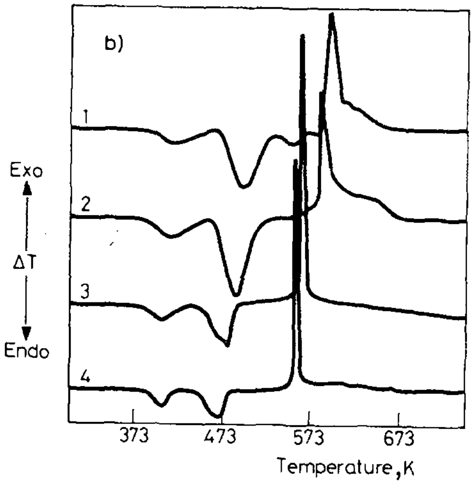

Fig. 2b DTA curves of the thermal decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$; in static air atmosphere. 1 - $\beta = 20$ deg min^{-1}, 2 - $\beta = 10$ deg min^{-1}, 3 - $\beta = 5$ deg min^{-1}, 4 - $\beta = 2$ deg min^{-1},

The DTA and DSC curves in Figs 1 and 2 illustrate the course of thermal decomposition of $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$. The kinetic parameters E and A for particular stages of the thermal decomposition were determined from the DTA, DTG and DSC curves by means of by Eq. (1). The linear regression parameters were estimated by using the least square method. The values of E, A and linear regression coeficient r are listed in Table 1. For comparison, values of E estimated from TG curves by means of the Arnold - Somogyvári - Paulik - Paulik (ASPP) method [14] (software of derivatograph C) are presented in Table 2. Limitations regarding this method have been presented in [14].

Table 1 Kinetic parameters calculated from the Kissinger equation (1)

Atmosphere	Stage	E, kJ mol^{-1}	log$A$, min^{-1*}	r
Argon (DTA)	I	93.1	11.3771	0.9959
	II	119.1	12.2455	0.9939
	III	183.4	15.1281	0.9996
Argon (DTG)	I	93.0	11.3696	0.9861
	II	120.2	12.3596	0.9849
	III	183.8	15.0520	0.9921
Air (DTA)	I	127.1	15.6000	0.9803
	II	130.2	13.4427	0.9904
	III	128.4	10.8568	0.9908
Air (DTG)	I	103.0	12.4254	0.9848
	II	136.0	14.0778	0.9968
	III	135.1	11.5027	0.9839
Air (DSC)	I	107.5	11.9576	0.9820
	II	131.3	13.3887	0.9970
	III	130.8	10.6106	0.9821

* pre-exponential factor unit

Table 2 Kinetic parameters calculated with the Arnold - Somogyvári - Paulik - Paulik method

Atmosphere	Stage	β, deg min^{-1}	E, kJ mol^{-1}	log$A$, min^{-1*}
Argon (TG-DTG)	I	2	93.7	11.0591
	II	2	133.8	13.5428
	III	2	185.6	14.7400
Air (TG-DTG)	I	2	126.4	15.0207
	II	2	132.5	13.3806
	III			

* pre-exponential factor unit

It can be seen from Table 1 that the E and A values for the first stage of dissociation estimated on the basis of the experimental DTG and DSC curves are close to each other. The corresponding values calculated from the DTA curves are somewhat higher. For the second and third stages, the E_{DTA}, A_{DTA} and E_{DSC}, A_{DSC} values are very close to each other. The E_{DTG} and A_{DTG} values are slightly higher.

In an argon atmosphere, the E and A values for all the stages of thermal decomposition of the ammine complex are nearly the same.

The E and A values calculated with the ASPP method (Table 2) are close to the corresponding values presented in Table 1.

The E values estimated for the first and second stages of dissociation in argon are slightly lower than in air.

For the third stage of dissociation, the E and A values determined in air and argon atmospheres are distinctly different, in accordance with the different courses of this stage in the two atmospheres (Eqs 4-6).

The experimental results presented above lead to the conclusion that the use of the experimental DTA, DTG or DSC curves for estimation of the kinetic parameters E and A by Kissinger's method gives rise to closely similar results.

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Zusammenfassung — Für verschiedene Schritte der thermischen Zersetzung von $[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$ in Luft bzw. Argon wurden nach dem Kissinger-Verfahren auf der Basis von DTA-, DTG- und DSC-Kurven Werte für die kinetischen Parameter E und A ermittelt. Es wurde gezeigt, daß das Kissinger-Verfahren für die verschiedenen Arten von experimentellen Kurven (DTA, DSC, DTG) genaue Ergebnisse liefert.