Journal of Thermal Analysis and Calorimetry, Vol. 69 (2002) 125–133

KINETIC ANALYSIS OF TG DATA XXXVI
Influence of procedural variables upon the apparent kinetic parameters of the thermal deamination

J. Zsakó, *I. Szilágyi*[2], *Á. Simay*[2], *Cs. Várhelyi*[1] *and K. Kerekes*[1]

[1]Faculty Chemistry and Chemical Engineering, Babeş-Bolyai University, Arany J. str. 11, 3400 Cluj, Romania
[2]Budapest University of Technology and Economics, Department of Inorganic Chemistry, 1521 Budapest, Hungary

Abstract

A number of 7 complexes of the [Co(DH)$_2$(amine)$_2$)]I type (DH$_2$ stands for dimethyloxime) have been studied by means of thermogravimetry and differential scanning calorimetry in nitrogen atmosphere, by using heating rates of 2.5, 5 and 10 K min^{-1}. In all cases an endothermal deamination reaction occurs leading to the relatively stable [Co(DH)$_2$I(amine)] intermediate. For this reaction apparent kinetic parameters have been derived. The influence of heating rate is discussed. The validity of a linear and a non-linear kinetic compensation law was verified.

Keywords: Co(III) complexes, DSC, influence of procedural variables, kinetic compensation effect, kinetics, TG

Introduction

The shape of the thermogravimetric (TG) curves are very much influenced by procedural variables as sample holder geometry and material, heating rate, atmosphere, sample mass, particle size, impurities, temperature measurement, construction of the apparatus and even prehistory of the sample [1].

Frequently, from the TG curves apparent kinetic parameters, viz. activation energy (*E*), pre-exponential factor (*A*) and reaction order (*n*) are derived. Between these parameters and the shape of the TG curves there is a definite correlation [2], consequently, apparent kinetic parameters depend on all the above mentioned procedural variables. Thus, the apparent activation energy of the dehydration of $CaC_2O_4 \cdot H_2O$ has been observed to decrease with increasing heating rate, with increasing sample mass and also by replacing the Pt plate sample holder by a Pt crucible [3]. Decreasing apparent activation energy with increasing heating rate has been reported with many thermal decomposition reactions [4–8].

In the case of complex thermal decomposition not only the apparent kinetic parameters, but also the number of decomposition stages, the position the mass loss stop

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

can be influenced by procedural variables. Thus, the pyrolysis of $Me^{II}L_2X_2$ type coordination compounds [9] at low heating rates obey the following scheme

$$Me^{II}L_2X_2 \rightarrow Me^{II}LX_2 \rightarrow Me^{II}L_{2/3}X_2 \rightarrow Me^{II}X_2 \quad (1)$$

but at higher heating rates it decomposes according to

$$Me^{II}L_2X_2 \rightarrow Me^{II}LX_2 \rightarrow Me^{II}X_2 \quad (2)$$

In our previous papers the thermal decomposition of several $M^{II}L_2X_2$ type complexes have been studied, viz. [Co(*m* = toluidine)$_2$Br$_2$][10], [Co(*m* = toluidine)$_2$Cl$_2$] [11] and [CoL$_2$(NCS)$_2$] with *L*=aniline, *m*-toluidine and *p*-toluidine, respectively [12]. TG measurements have been performed under 12 different working conditions each, by using 3 different heating rates (5, 10 and 15 K min^{-1}) and 4 different sample masses (25, 50, 75 and 100 mg). As observed, the apparent kinetic parameters derived for the first thermal decomposition stage showed a systematic variation. Thus, the apparent reaction order increased both with increasing heating rate and increasing sample mass. Oppositely, *E* and *A* decreased with increasing heating rate and increasing sample mass.

A similar effect has been observed with [Co(en)$_2$(amine)X]Y$_2$ type complexes [13–15]. The first pyrolysis stage of these complexes consists of the following deamination reaction:

$$[Co(en)_2(amine)X]Y_2 \rightarrow [Co(en)_2XY]Y + \text{amine} \quad (3)$$

By performing the TG analysis of 7 [Co(en)$_2$(amine)X]Y$_2$ type complexes, under the same 12 different experimental conditions as mentioned above, one observed both the apparent activation energy and pre-exponential factor to decrease with increasing sample mass, as well as with increasing heating rate. With respect to the apparent reaction order the effect of the working conditions is not so clear. Frequently, increasing sample mass and increasing heating rate entail the increase of *n*, but sometimes exactly the opposite effect is observed.

The explanation of the above effects of working conditions upon the apparent kinetic parameters seems to be rather simple. A linear variation of the furnace temperature is ensured, but the actual temperature in the sample is not the same. Since the heat conduction has a finite rate, a temperature lag appears between the furnace and the sample. The higher the heating rate, the larger this temperature lag. On the other hand, the volatilization of the evolved gaseous product is not instantaneous and it implies also a diffusion process across the superior layers of the sample. Both the temperature lag and the hindering of the evolution of the gaseous product slow down the rate of mass loss, the TG curve becomes flatter and the temperature interval of the decomposition stage increases [16]. With increasing sample mass and increasing rate these effects become more important. By taking into account the correlation between the shape of the TG curves and the apparent kinetic parameters [2], this effect is equivalent with decreasing of the apparent activation energy.

As far as the apparent reaction order is concerned, it is also correlated with the shape of the TG curve. Based on the master curves, suggested by Ozawa [17], we proposed the following shape parameter for TG curves [18]:

$$\nabla=\frac{\vartheta_{0.5}-\vartheta_{0.9}}{\vartheta_{0.1}-\vartheta_{0.9}} \tag{4}$$

where ϑ_α stands for $1/T_\alpha$, T_α meaning the temperature at which the conversion attains the value α (i.e. 0.1, 0.5 and 0.9, respectively). This parameter is a unique function of the apparent reaction order. Thus, from its experimental value n can be simply calculated [15, 18].

As seen from (4), ∇ and therefore also n depends on the relative extent of the temperature interval in which the second half of the decomposition stage occurs. With increasing n, the temperature interval between $\alpha=0.5$ and 0.9 exhibits a more important increase as compared to the interval between $\alpha=0.1$ and 0.5. Generally, the diffusion of the gaseous product is more hindered in the second half of the decomposition stage, which in terms of kinetic parameters means that n increases with both increasing sample mass and increasing heating rate. Nevertheless, it may happen, that the solid product of the pyrolysis process has a loose structure and the diffusion is more hindered even at the beginning of the decomposition. In this case n will decrease with increasing sample mass and heating rate [12].

Another deamination reaction, leading to the formation of a relatively stable intermediate product has been observed with $[Co(DioxH)_2(amine)_2]X$ type complexes [19–22], where $DioxH_2$ stands for an α-dione-dioxime, amine is an aromatic or heterocyclic amine and X stands for a halogene or pseudohalogene anion. The first decomposition stage consists of the following reaction:

$$[Co(DioxH)_2(amine)_2]X \rightarrow [Co(DioxH)_2X(amine)]+amine \tag{5}$$

The influence of heating rate upon the apparent kinetic parameters has been studied in the case of a number of 21 $[Co(DH)_2(amine)_2]SCN$ type complexes [16] and a number of 22 $[Co(DH)_2(amine)_2]I$ type complexes [23], where DH_2 stands for dimethylglyoxime [16]. With increasing heating rate a systematic decrease of both E and A has been observed.

Several complexes of this type have been studied under 12 different working conditions, viz. by using heating rates of 5, 10 and 15 K min^{-1}, as well as sample masses of 25, 50, 75 and 100 mg, respectively. The complexes studied contained alycyclic dione-dioximes as cyclohexane-dione-dioxime ($NioxH_2$) [24], cycloheptane-dione-dioxime ($HeptoxH_2$) and cyclooctane-dione-dioxime ($OctoxH_2$), respectively [25]. Similarly to the other substances studied, the decrease of both E and A has been observed with increasing heating rate and also with increasing sample mass. The apparent reaction order exhibited a decreasing tendency with both increasing heating rate and increasing sample mass, suggesting the idea that diffusion is hindered mainly at the beginning of the pyrolysis.

In the present paper several $[Co(DH)_2(amine)_2]I$ type complexes are studied by means of TG and DSC measurements.

Experimental

Synthesis of the $[Co(DH)_2(amine)_2]I$ type complexes

A mixture of $(CH_3COO)Co$, of dimethylglyoxim and of the corresponding amine in a molar ratio of 1:2:2.5, dissolved in ethanol of 50–70% is oxidized by air bubbling, or with H_2O_2. The iodides are obtained from the resulting brown solutions by means of double exchange reaction with NaI or KI. The products have been identified and characterized by chemical analysis and their middle IR spectra.

Thermal investigations

TG, DTG and heat flow (HF) curves of 5–6 mg samples have been recorded in nitrogen atmosphere at heating rates of 2.5, 5 and 10 K min^{-1}, respectively, by using a 951-TG and 910-DSC calorimeter (DuPont Instruments).

Results and discussions

The following $[Co(DH)_2(amine)_2]I$ type complexes have been synthesized:

I.	$[Co(DH)_2(aniline)_2]I{\cdot}H_2O$
II.	$[Co(DH)_2(amine)_2(p\text{-chlor-aniline})_2]I$
III.	$[Co(DH)_2(o\text{-toluidine})_2]I$
IV.	$[Co(DH)_2(m\text{-toluidine})_2]I$
V.	$[Co(DH)_2(p\text{-toluidine})_2]I$
VI.	$[Co(DH)_2(o\text{-anisidine})_2]I$
VII.	$[Co(DH)_2(m\text{-xylidine})_2]I$

where DH_2 stands for dimethyl-glyoxime.

Samples of 5–6 mg have been submitted to a TG-DSC analysis in nitrogen atmosphere, by using a platinum container and heating rates of 2.5, 5 and 10 K min^{-1}, respectively. TG, DTG and HF curves have been recorded at room temperature up to 650 K. In this temperature range complexes II–VII exhibited 3 decomposition stages, the compound I one more stage corresponding to the loss of crystallization water. Let us denote this dehydration as stage 1, which occurs only with compound I and the mass loss corresponds exactly to 1 mole H_2O. As shown by the HF curve, this process is an endothermal one.

Stage 2 is observed with all complexes studied and can be characterized also by a clear stoichiometry. The mass loss corresponds to 1 mole amine, i.e. this process is the substitution reaction (5), leading to the formation of the non-electrolytic compound $[Co(DH)_2I(amine)]$ and to the volatilization of the liberated amine. As shown by the HF curves, this deamination is also an endothermal process.

Stage 3 has no clear stoichiometry. Generally, the mass loss exceeds 1 mole of amine, i.e. this is not a simple deamination process and also the $Co(DH)_2$ moiety is involved. Presumably, it is an intramolecular redox reaction, since the atmosphere is inert but the HF curves indicate an exothermal process.

Stage 4 exhibits a smaller mass loss, but an even more important exothermal effect.

The characteristics of the HF curves are presented in Table 1.

Table 1 Endothermal DSC peak temperatures of stages 1 and 2 and exothermal DSC peak temperatures for stages 3 and 4

Compound	Q/K min^{-1}	Stage 1	Stage 2	Stage 3	Stage 4
I	2.5	337.4	438.4	513.4	543.7
	5	351.9	444.1	515.8	551.8
	10	344.6	451.5	517.5	558.1
II	2.5	–	449.3	514.0	544.7
	5		442.7	519.6	555.2
	10		445.1	521.0	559.0
III	2.5	–	432.4	505.1	542.8
	10		437.3	510.7	556.6
IV	2.5	–	448.2	494.2	543.6
	5		453.0	498.1	570.7
	10		456.8	501.0	560.5
V	2.5	–	468.0	516.7	544.5
	5		472.4	522.6	555.4
	10		477.4	523.4	560.7
VI	2.5	–	461.2	521.0	541.5
	5		462.5	526.6	551.4
	10		463.3	529.9	549.3
VII	2.5	–	442.9	509.8	544.5
	5		442.3	511.3	558.3
	10		443.0	512.0	562.0
General mean for I–VII	2.5	–	448.6	510.6	543.6
	5		452.8	515.7	557.1
	10		453.5	516.8	558.0

As seen from Table 1, with increasing heating rate the DSC peak temperatures are shifted towards higher temperatures. This is clear evidence of the role of heat conduction and it tells nothing else other than that due to the finite rate of heat conduction with increasing heating rate increases the temperature lag between the furnace and sample.

In the case of stage 2 the regular shape of the TG curves allowed us to derive kinetic parameters. For this purpose our nomogram method [26] was used. The characteristic temperatures $T_{0.1}$, $T_{0.5}$ and $T_{0.9}$, corresponding to the coversions α=0.1, 0.5 and 0.9, respectively, were derived from the experimental TG curves. These temperatures are presented in Table 2.

The general picture is similar to that observed with the DSC peak temperatures, i.e. all characteristic temperatures show an increasing tendency with increasing heating rate, due to the finite rate of the heat conduction.

Table 2 Characteristic temperatures of reaction (5)

Compound	Q/K min^{-1}	$T_{0.1}$	$T_{0.5}$	$T_{0.9}$/°C
I	2.5	423.0	436.5	445.9
	5	428.4	439.2	450.0
	10	431.1	444.6	456.1
II	2.5	433.1	446.6	461.5
	5	435.1	445.9	449.3
	10	436.5	445.3	448.0
III	2.5	421.6	429.7	439.2
	10	423.0	436.5	451.9
IV	2.5	431.7	445.9	454.7
	5	438.1	452.2	462.0
	10	441.0	453.1	464.1
V	2.5	452.4	464.2	474.3
	5	457.4	465.9	477.0
	10	464.2	475.0	485.1
VI	2.5	437.8	455.0	463.5
	5	438.1	455.5	464.2
	10	439.2	456.1	466.2
VII	2.5	435.1	441.9	448.0
	5	433.8	443.2	447.6
	10	429.7	441.9	446.0
General mean of I–VII	2.5	433.5	445.7	455.3
	5	438.5	450.3	457.8
	10	437.8	450.4	459.6

The shape and position parameters, defined as

$$\nabla=\frac{\vartheta_{0.5}-\vartheta_{0.9}}{\vartheta_{0.1}-\vartheta_{0.9}};\quad \Delta=10^{6}(\vartheta_{0.1}-\vartheta_{0.5});\quad \tau=10^{3}\vartheta_{0.1} \tag{6}$$

have been calculated by using the characteristic temperatures given in Table 2, these parameters are presented in Table 3.

By means of the shape and position parameters and the nomogram given in [26], the first approximation of the kinetic parameters n, E and lg$A$ have been obtained, which allowed us to calculate, by means of the empirical formulae given in [27], the reduced shape and position parameters ∇^*, Δ^* and τ^*. By using the proposed iterative procedure, eventually the apparent kinetic parameters have been obtained. These are presented also Table 3.

Inspection of Table 3 shows the influence of heating rate upon the apparent kinetic parameters not to be quite clear. Not even the systematic decrease of E with increasing heating rate, reported in our earlier papers and also by many other authors, is not observed in this case. Since the above mentioned effect seems to be due to the hindering of diffusion of the gaseous product across the sample, one may presume that with diminishing sample mass the role of diffusion becomes less important and the kinetic parameters are influenced also by other aleatory variables.

Table 3 Shape (∇, Δ) and position (τ) parameters of the TG curve and apparent kinetic parameters derived

Comp.	Q/ K min^{-1}	τ	Δ	∇	n	E/ kJ mol^{-1}	lg$A$	lgA^*
I	2.5	2.364	73.1	0.3978	1.08	207.6	22.5	22.5
	5	2.334	57.4	0.4877	1.89	303.1	34.6	34.2
	10	2.320	70.4	0.4460	1.50	232.7	25.3	25.7
II	2.5	2.309	69.80	0.5088	2.09	256.2	27.2	27.8
	5	2.298	55.67	0.2336	–0.26	221.9	23.6	23.8
	10	2.291	45.27	0.2301	–0.29	271.3	30.0	30.0
III	2.5	2.372	44.71	0.5296	2.18	109.7	10.7	10.2
	10	2.364	73.11	0.5164	2.07	176.6	19.1	19.2
IV	2.5	2.316	73.77	0.3704	0.84	197.2	21.2	20.7
	5	2.283	71.17	0.3973	0.98	170.0	17.3	17.3
	10	2.268	60.56	0.4635	1.50	239.5	25.7	25.8
V	2.5	2.210	56.19	0.4495	1.43	186.3	17.6	18.2
	5	2.186	39.89	0.5560	2.31	213.5	21.5	21.5
	10	2.154	48.98	0.4723	1.74	344.5	36.5	36.3
VI	2.5	2.284	86.35	0.3182	0.37	149.9	14.4	14.5
	5	2.283	87.19	0.3206	0.38	118.0	10.7	10.9
	10	2.277	84.37	0.3602	0.75	170.4	17.6	17.6
VII	2.5	2.298	35.37	0.4656	1.68	486.4	54.8	55.6
	5	2.305	48.89	0.3121	0.36	228.3	24.1	24.6
	10	2.327	64.25	0.2446	–0.21	193.8	21.0	21.0
General mean I–VII	2.5	2.308	–	–	1.38	227.6	23.6	–
	5	2.281			0.89	209.1	22.0	
	10	2.286			1.11	232.6	25.0	

It is interesting to compare the mean value of the apparent activation energy obtained in the present paper with those reported earlier for the deamination of other [Co(DioxH)$_2$(amine)$_2$]X type complexes, by using larger samples. These data are presented in Table 4.

Table 4 Mean values of the apparent activation energy as function of the sample mass

Sample mass/mg	E/kJ mol^{-1}	Number of experimental data	References
100	137.2	136	[16], [23–25]
75	151.9	21	[24], [25]
50	169.0	21	[24], [25]
25	195.6	21	[24], [25]
5–6	223.1	20	this paper

Obviously, with decreasing sample mass increases the apparent activation energy, which means that the part of the diffusion diminishes in agreement with our above supposition.

Further, inspection of Table 3 shows that with increasing E a systematic increase of lg$A$ may be observed as the manifestation of the so-called kinetic compensation effect. Frequently, this compensation effect obeys a linear law:

$$\lg A = aE + b \tag{7}$$

which is called also isokinetic relation, since if there is a certain temperature T_i (isokinetic temperature), at which in a set of reactions all the rate constants have the same value (k_i), from the Arrhenius' equation one has:

$$\lg A = \frac{E}{2.3RT_i} + \lg k_i \tag{8}$$

As shown earlier [28], in TG kinetics Eq. (8) is valid for thermal decomposition stages with the characteristic temperatures $T_{0.1}$ comprised in a sufficiently narrow interval. In this case T_i is very near to $T_{0.1}$ and lgk_i is approximately equal to –3. Since $T_{0.1}$ of the deamination reactions studied in the present paper are comprised between 423 and 457 K (Table 2) we verified the validity of Eq. (8). By means of linear regression one obtained T_I=442 K (the mean value of $T_{0.1}$ is 436.6 K) and lgk_i=–2.66 in a good agreement with the above findings and with a correlation coefficient of r=0.9967, indicating a quite good linearity.

We tested also a non-linear compensation law proposed earlier [28], viz.

$$\lg A^* = \frac{E}{RT_{0.1}\ln 10} + \lg\frac{qE}{T_{0.1}^2} - 1.85 \tag{9}$$

The lgA^* values calculated from the experimental q, E and $T_{0.1}$ values by using Eq. (9) are presented above in Table 3. Obviously, lgA^* values are in good agreement with lg$A$ values derived directly from the TG curves. In order to characterize this agreement, we performed a lgA^* *vs.* lg$A$ plot and by means of linear regression we calculated the parameters of the straight line obtained. One has an ordinate intercept of –0.16 instead of 0 and a slope of 1.011 instead of 1, corresponding to a perfect agreement. Consequently, the agreement may be considered to be quite good and the correlation coefficient of 0.9995 shows, that even in narrow $T_{0.1}$ interval Eq. (9) ensures a better description of the compensation effect, than Eq. (8) does.

In order to obtain some pieces of information concerning the possible thermal decomposition processes, the mass spectrum of [Co(DH)$_2$(o-toluidine)$_2$]I has been recorded. In the $100 \le M/z \le 550$ range the most intensive line (100%) appears at 288 corresponding to the planar Co(DH)$_2$ moiety, which has particular stability due to intramolecular hydrogen bridges. One has also the lines of Co(DH)$_2$(o-toluidine)$_2$ at 503 (26.5%), of Co(DH)$_2$(o-toluidine) at 397 (14.8%) and of o-toluidine at 107 (33.4%). These results show that at the thermal decomposition of similar complexes a (5) type substitution reaction might occur indeed, but they can tell nothing about the mechanism of this reaction, of its S_N1 or S_N2 character.

References

1 C. J. Keattch, An Introduction to Thermogravimetry, Heyden and Son Ltd., London, Sadtler Research Laboratories Inc., Philadelphia 1969, p. 21.
2 J. Zsakó, J. Chim. Phys., 66 (1969) 1041.
3 J. Simon, J. Thermal Anal., 5 (1973) 271.
4 R. C. Turner, J. Hoffmann and D. Chen, Canadian J. Chem., 41 (1963) 243.
5 D. Furnica and J. A. Schneider, Makromol. Chem., 108 (1967) 182.
6 J. A. Schneider, C. Vasile, D. Furnica and A. Onu, Makromol. Chem., 117 (1968) 41.
7 C. N. Caşcaval, C. Vasile and J. A. Schneider, Makromol. Chem., 131 (1970) 55.
8 J. C. Hisatsune, E. C. Beahm and R. J. Kempf, J. Phys. Chem., 74 (1970) 3444.
9 I. G. Murgulescu, D. Fătu and E. Segal, J. Thermal Anal., 1 (1969) 97.
10 J. Zsakó, E. Kékedy and Cs. Várhely, Proc. 3rd ICTA, Davos 1971, p. 487.
11 J. Zsakó, Cs. Várhelyi and E. Kékedy, Proc. 4th ICTA, Budapest 1974, p. 177.
12 J. Zsakó, Cs. Várhelyi, B. Csegedi and J. Zsakó, Thermochim. Acta, 45 (1981) 11.
13 J. Zsakó, M. Várhelyi and Cs. Várhelyi, J. Thermal Anal., 17 (1979) 123.
14 J. Zsakó, Cs. Várhelyi and S. Magyarósi, Studia Univ. Babeş-Bolyai, Chem., 26 (1981) 52.
15 J. Zsakó, Gh. Marcu and M. Várhelyi, Rev. Roum. Chim., 27 (1982) 815.
16 J. Zsakó, E. Kékedy and Cs. Várhelyi, J. Thermal Anal., 1 (1969) 339.
17 T. Ozawa, Bull. Chem. Soc. Japan, 38 (1965) 1881.
18 J. Zsakó, Rev. Roum. Chim., 15 (1970) 693.
19 J. Zsakó, Cs. Várhelyi and E. Kékedy, Studia Univ. Babeş-Bolyai, Chem., 10 (1965) 7; Anal. Univ. Bucureşti, Chim., 14 (1965) 15; Proc. Anal. Chem. Conf., Budapest 1966, 353; J. Inorg. Nucl. Chem., 28 (1966) 2637; 32 (1970) 2999; Zh. Neorg. Khim., 13 (1968) 3279.
20 J. Zsakó, J. Phys. Chem., 72 (1968) 2406.
21 J. Zsakó, Cs. Várhelyi and G. Liptay, Proc. 4th ICTA, Budapest 1974, p. 825.
22 J. Zsakó, Cs. Várhelyi Jr., G. Marcu and G. Liptay, J. Therm. Anal. Cal., 55 (1999) 311.
23 J. Zsakó, E. Kékedy and Cs. Várhelyi, Rev. Roum. Chim., 15 (1970) 865.
24 J. Zsakó, J. Horák and Cs. Várhelyi, J. Thermal Anal., 20 (1981) 435.
25 J. Zsakó, J. Horák, Cs. Várhelyi and A. Benkő, Monatshn., 112 (1981) 945.
26 J. Zsakó, J. Thermal Anal., 15 (1979) 369.
27 J. Zsakó, J. Thermal Anal., 47 (1996) 1679.
28 J. Zsakó, J. Therm. Anal. Cal., 54 (1998) 921.