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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA XIII. THERMAL DECOMPOSITION OF COMPLEXES OF TYPE $[Co(en)_2(pyridine)Cl]X_2$

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Kinetic parameters of the dehydration of $ACl_2.1.5\ H_2O$, and of the substitution of pyridine by the outer sphere anion, have been derived from the TG curves of $ACl_2.1.5\ H_2O$, ABr_2 and AI_2 ($A = [Co(en)_2(pyridine)Cl]$) by using the author's nomogram method and the Coats-Redfern method. The influences of sample weight and of heating rate have been studied. Statistical analysis of the results shows the apparent activation energy E of the substitution reaction to decrease in the order Cl > Br > I, while both E and the pre-exponential factor values decrease with increasing sample weight and increasing heating rate. The kinetic compensation effect is discussed.

The thermal decompositions of $ACl_2 \cdot 1.5\ H_2O$, ABr_2 and AI_2 ($A = [Co(en)_2(pyridine)Cl]$, *en* = ethylenediamine) have been studied in a platinum crucible by means of a thermobalance [1], by using a linear temperature program with the constant heating rates $q = 5$, 10 and 15 K min^{-1}. Sample weights used were 25, 50, 75 and 100 mg, respectively.

A typical TG curve of each compound studied is given in Fig. 1.

The first stage of the thermal decomposition of $ACl_2.1.5\ H_2O$ is dehydration, corresponding to the loss of 1.5 moles of crystallization water. The second stage is deamination, the weight loss corresponding to 1 mole of pyridine. Presumably the pyridine molecule is substituted by an outer sphere Cl^- ion and $[Co(en)_2Cl_2]Cl$ is formed as intermediate, but its further decomposition begins fairly soon, since no plateau is obtained in the TG curve. In the cases of the other two compounds, the first stage is a similar deamination, leading to the formation of $[Co(en)_2BrCl]Br$ and $[Co(en)_2ICl]I$ intermediates, the latter being relatively stable.

Derivation of kinetic parameters

In order to characterize the TG curves obtained, the kinetic parameters apparent reaction order n, activation energy E and pre-exponential factor Z have been derived. Two methods have been used, the nomogram method proposed in our previous paper [2], and the Coats–Redfern method [3], modified as described below.

By using the experimentally-obtained time-weight pairs, the TG curves have been constructed, separately for each thermal decomposition stage, by plotting the fraction of compound not transformed, $1 - \alpha$, versus temperature (α is the transformation degree or conversion).

In the case of the nomogram method, the quantities $\vartheta_{0.1}$, $\vartheta_{0.5}$ and $\vartheta_{0.9}$ (the reciprocal absolute temperature values corresponding to the conversion values $\alpha = 0.1$, 0.5 and 0.9, respectively) have been determined graphically, by using the above-mentioned TG curves. The shape and position parameters

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

have been calculated and used for the determination of kinetic parameters as described in [2]. Since the heating rates were very close (or even identical) to the value 10 K min^{-1}, taken as standard in the construction of the nomogram, two iteration cycles were sufficient; i.e. the second approximations could be taken as final values. The use of the nomogram given in [2], raises some interpolation problems, since a linear interpolation cannot be satisfactory due to the decreasing distance between the curves E = const. and $\log Z$ = const., with increasing E and

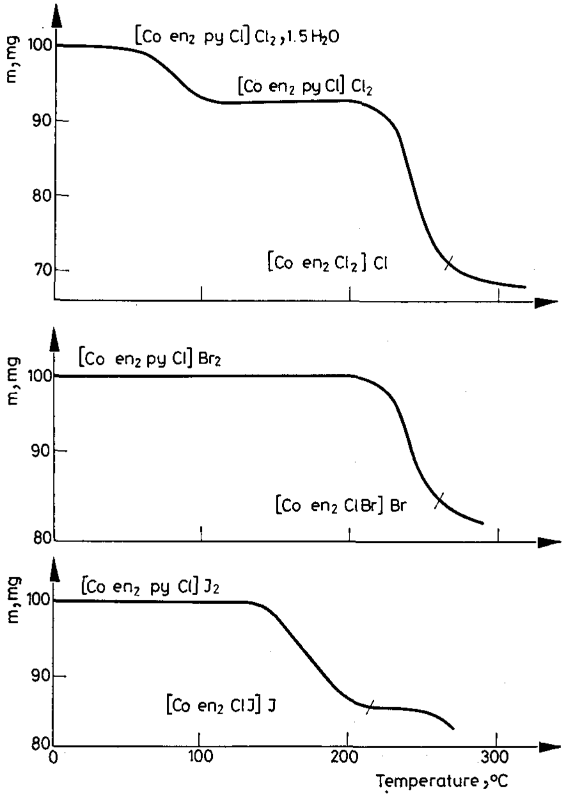

Fig. 1. Typical TG curves of complexes of type [Co(en)$_2$(pyridine)Cl]X$_2$

Z. In order to make possible a non-linear interpolation, an interpolation curve has been constructed, taking into account the mean value of the ratio of the distances between two successive curves. Let us consider two successive curves, corresponding to E_i and E_j, and suppose that the reduced parameters Δ^* and τ^* (see [2]) obtained for the TG curve determine a point on the nomogram, situated between the two curves considered, viz. at a distance d_i from the curve E_i and d_j from the curve E_j. The activation energy corresponding to this point will be

$$E = E_i + D(E_j - E_i) \tag{1}$$

If a linear interpolation were possible, the coefficient D would be equal to

$$D_L = \frac{d_i}{d_i + d_j} \tag{2}$$

Our interpolation curve is a plot of D versus D_L and it can be constructed by using the D and D_L values presented in Table 1.

Table 1

Some points of the interpolation curve

D_L	D	D_L	D	D_L	D
0.00	0.0000	0.35	0.2630	0.70	0.6118
0.05	0.0332	0.40	0.3070	0.75	0.6702
0.10	0.0677	0.45	0.3528	0.80	0.7309
0.15	0.1037	0.50	0.4005	0.85	0.7942
0.20	0.1412	0.55	0.4502	0.90	0.8600
0.25	0.1801	0.60	0.5019	0.95	0.9286
0.30	0.2207	0.65	0.5557	1.00	1.0000

Thus, E values are obtained easily by means of formula (1). The interpolation between two successive curves, $\log Z_i$ and $\log Z_j$, can be performed in the same manner, by using the same interpolation curve and the relation

$$\log Z = \log Z_i + D(\log Z_j - \log Z_i) \tag{3}$$

As far as the application of the Coats–Redfern method is concerned, the TG curves (plot of $(1 - \alpha)$ vs. T) have been used to determine 9 temperature values, corresponding to $\alpha = 0.1, 0.2, 0.3, \ldots, 0.8$ and 0.9. For these α' values the conversion integral

$$g(\alpha') = \int_0^{\alpha'} \frac{d\alpha}{(1 - \alpha)^n} \tag{4}$$

has been calculated and tabulated by taking $n = 0, 0.1, 0.2, 0.3, \ldots$ up to $n = 4.0$. By using the above determined 9 temperature values, $\log [g(\alpha')/T^2] - 1/T$ pairs have been calculated, for different n values. In order to obtain the correct n value, the least squares method has been used, viz. the equation of the straight line determined by the nine log $[g(\alpha')/T^2] - 1/T$ pairs has been calculated and Jaffé's correlation coefficient (ρ) has been calculated [4]. The graphical plot of ρ vs. n allowed us to determine the maximum of ρ, and the corresponding abscissa has been taken as the most probable n value.

Results and discussion

Kinetic parameters derived by means of both methods are presented in Tables 2–5. Values obtained by means of the Coats–Redfern method are denoted as n_{CR}, E_{CR} and log Z_{CR} respectively. As seen from these Tables, both methods give nearly the same values for all kinetic parameters. As regards influences of heating rate and sample weight, no systematic variation of the kinetic parameters can be observed. Generally, the values obtained are rather scattered. Only the position parameter τ^* has a practically constant value.

In order to obtain a clearer picture, a statistical analysis of the data obtained has been performed. For this purpose, mean values of the kinetic parameters have been calculated separately for each reaction, for the sample weights and heating rates used.

The general mean value, i.e. the arithmetical mean of all values obtained, irrespective of reaction, sample weight or heating rate, shows clearly that the two methods used are of the same value, since they give practically the same results.

Table 2

Kinetic parameters of thermal dehydration of *cis*-$[Co(en)_2(pyridine)Cl]Cl_2.1.5H_2O$

Heating rate, K min^{-1}	Sample weight, mg	n	n_{CR}	E, kcal mol^{-1}	E_{CR}, kcal mol^{-1}	log Z	log Z_{CR}	τ^*
5	25	0.62	0.73	19.5	19.8	10.6	10.8	3.131
	50	1.26	1.32	28.5	28.0	16.6	16.3	3.098
	75	1.11	1.15	22.4	21.8	12.1	11.6	3.005
	100	1.40	1.37	28.3	27.1	16.1	15.2	3.017
10	25	1.43	1.43	34.3	34.0	20.8	20.6	3.110
	50	1.43	1.37	18.5	17.3	9.9	9.0	3.127
	75	1.36	1.27	22.6	20.8	12.4	11.1	3.052
	100	0.90	0.96	17.4	17.1	8.6	8.5	3.028
15	25	1.19	1.23	36.1	36.0	21.6	21.6	3.069
	50	1.56	1.50	29.2	27.6	16.6	15.6	3.017
	75	1.52	1.45	23.0	20.3	12.9	10.9	3.066
	100	1.28	1.26	21.2	20.7	11.3	11.0	3.032

On the other hand, it is obvious that increasing sample weight diminishes E and $\log Z$ values, and the same effect is observed with increasing heating rate. This means simply that, with increasing sample weight and heating rate, the temperature interval corresponding to the thermal decomposition increases.

Table 3

Kinetic parameters of thermal deamination of *cis*-[Co(*en*)$_2$(pyridine)Cl]Cl$_2$

Heating rate, K min^{-1}	Sample weight, mg	n	n_{CR}	E, kcal mol^{-1}	E_{CR} kcal mol^{-1}	$\log Z$	$\log Z_{CR}$	τ^*
5	25	2.96	3.30	167.5	180.7	71.6	78.0	2.029
	50	1.63	1.68	103.6	112.2	43.7	47.7	2.041
	75	3.39	3.87	181.2	183.3	77.0	81.6	2.018
	100	1.86	1.90	86.5	92.7	36.3	39.0	2.045
10	25	3.20	3.40	161.0	153.4	69.0	65.6	2.023
	50	2.37	2.34	105.5	98.9	44.6	41.4	2.027
	75	2.60	2.61	119.7	108.6	50.4	45.9	2.034
	100	2.22	2.23	121.7	114.9	50.7	48.0	2.006
15	25	2.13	2.13	109.8	112.8	45.8	46.9	2.001
	50	1.73	1.71	100.0	95.5	41.2	39.8	2.024
	75	1.47	1.47	101.8	99.0	41.7	40.7	1.994
	100	2.32	2.30	82.8	78.6	33.7	31.8	2.002

Table 4

Kinetic parameters of thermal deamination of *cis*-[Co(*en*)$_2$(pyridine)Cl]Br$_2$

Heating rate, K min^{-1}	Sample weight, mg	n	n_{CR}	E, kcal mol^{-1}	E_{CR} kcal mol^{-1}	$\log Z$	$\log Z_{CR}$	τ^*
5	25	1.04	0.91	87.1	86.4	35.4	35.0	1.986
	50	0.76	0.75	96.6	96.4	40.3	40.2	2.026
	75	0.66	0.62	94.2	95.4	38.9	39.5	2.011
	100	1.34	1.51	105.6	114.4	44.3	48.1	2.016
10	25	1.25	1.27	92.3	97.8	37.7	40.3	1.998
	50	1.52	1.45	90.4	87.9	37.0	36.1	2.011
	75	0.96	0.92	71.2	72.4	28.4	29.0	1.997
	100	1.12	1.06	70.2	70.1	28.3	28.3	2.017
15	25	1.77	1.71	99.1	95.3	40.4	38.8	1.984
	50	2.08	2.09	100.5	101.1	41.1	41.8	2.000
	75	0.61	0.63	47.6	48.4	18.2	18.6	2.021
	100	2.26	2.39	105.0	114.6	43.1	47.3	1.983

Table 5

Kinetic parameters of thermal deamination of *cis*-[Co(*en*)$_2$(pyridine)Cl]I$_2$

Heating rate, K min^{-1}	Sample weight, mg	n	n_{CR}	E, kcal mol^{-1}	E_{CR}, kcal mol^{-1}	log Z	log Z_{CR}	τ^*
5	25	1.62	1.59	37.0	36.1	16.4	15.8	2.350
	50	1.94	1.87	40.2	37.9	17.6	16.5	2.322
	75	2.07	2.01	33.7	31.3	14.6	13.3	2.354
	100	1.58	1.55	34.4	31.9	14.8	13.5	2.337
10	25	2.15	2.15	32.3	31.1	13.7	13.2	2.359
	50	2.28	2.31	34.8	34.5	15.5	15.2	2.381
	75	0.97	0.98	22.4	22.6	8.6	8.6	2.346
	100	1.65	1.65	32.3	30.4	14.1	13.0	2.386
15	25	1.55	1.52	29.2	27.9	12.4	11.5	2.384
	50	1.80	1.81	31.2	31.5	13.2	13.2	2.345
	75	1.26	1.26	20.7	20.5	8.1	7.7	2.426
	100	0.97	1.01	21.1	20.9	8.2	7.9	2.410

Table 6

Mean values of the kinetic parameters

	n	n_{CR}	E, kcal mol^{-1}	E_{CR}, kcal mol^{-1}	log Z	log Z_{CR}	τ^*
dehydration of $ACl_2.1.5H_2O$	1.26	1.25	25.1	24.2	14.1	13.5	3.063
deamination of ACl_2	2.32	2.41	120.1	119.2	50.5	50.5	2.020
deamination of ABr_2	1.28	1.28	89.1	90.0	36.1	36.9	2.004
deamination of AI_2	1.65	1.64	30.8	29.7	13.1	12.5	2.367
25 mg sample	1.74	1.78	75.4	75.9	32.9	33.2	2.368
50 mg sample	1.70	1.68	64.9	64.0	28.1	27.7	2.368
75 mg sample	1.50	1.46	63.4	62.1	26.9	26.5	2.360
100 mg sample	1.57	1.64	60.6	61.1	25.8	26.0	2.357
5°/min heating rate	1.58	1.63	72.9	74.7	31.6	32.6	2.362
10°/min heating rate	1.71	1.71	65.4	63.2	28.1	27.1	2.369
15°/min heating rate	1.59	1.59	59.9	59.4	25.6	25.3	2.360
general mean	1.63	1.64	66.1	65.8	28.4	28.3	2.363

The explanation of this effect, observed in our previous papers too, could be simply the limitation of the heat transfer or of the diffusion rate of the gaseous product evolved.

The mean values calculated for the four decomposition reactions are rather different from one other. Both E and $\log Z$ values for the deamination reactions decrease very much in the order Cl > Br > I. This result is very important, because it shows that the kinetic parameters E and Z do have some real physical significance, related to the chemical reaction occurring.

It is true that the individual values of the kinetic parameters are affected very much by the working conditions (controlled and uncontrolled ones) and this is why the data presented in Tables 2–5 are scattered. Nevertheless, the mean values for several runs performed under the same conditions for the three complexes studied are rather different (Table 6). The decrease of the mean activation energy in the above order means the decrease of the real activation energy of the deamination reaction.

As seen from Tables 2–6, E and $\log Z$ values vary in parallel. The validity of a linear kinetic compensation law of the type

$$\log Z = aE + b \tag{5}$$

has been tested separately for the 4 reactions studied, by using the least squares method. The results are presented in Table 7.

Table 7

Kinetic compensation parameters

Reaction	a	b	ρ	a'
dehydration of $ACl_2.1.5\ H_2O$	0.688	−3.126	0.998	0.669
deamination of ACl_2	0.452	−3.544	0.999	0.441
deamination of ABr_2	0.441	−2.778	0.999	0.438
deamination of AI_2	0.516	−2.836	0.998	0.517

The high values of Jaffé's correlation coefficient ρ show a very good linearity.

As for as the interpretation of this kinetic compensation effect is concerned, our earlier hypothesis [6] is not entirely verified. To a first approximation, the stronger the chemical bond to be broken, the higher the compensation parameter a, as presumed earlier [6]. Thus, the highest value is obtained for the dehydration reaction. In the case of the deamination reactions, the Co–py bond can be weakened by a polarization effect and this explains the high a value of the AI_2 decomposition. However, the higher a value for ACl_2 as compared to ABr_2 is not consistent with our hypothesis.

On the other hand, Garn [7] presumes this parameter a to represent simply $\frac{\log e}{RT_c}$, where T_c stands for a certain decomposition temperature. By taking for

$1/T_c$ the reduced position parameter τ^*, the $a' = (\tau^* \log e)/R$ values have been calculated and are given in Table 7. As seen from this Table, the values of a and a' are quite close to each other, i.e. to some extent Garn's hypothesis seems to be correct and the compensation parameter a might be related to a standard decomposition temperature represented to a first approximation by the reduced position parameter τ^*.

Experimental

Synthesis of cis-[Co(*en*)$_2$Cl(pyridine)]X$_2$ *complex salts*

28.5 g (0.1 mole) *trans*-[Co(*en*)$_2$Cl$_2$].Cl is dissolved in 100 ml water and 9.0 g (0.11 mole) of pyridine is added drop by drop. The green solution gradually becomes violet-red. After standing about 24 hr it is filtered [8].

30 ml of this solution is mixed with an excess of concentrated aqueous solution of 50 – 60 g NH_4Cl.

The *cis*-[Co(*en*)$_2$Cl(pyridine)]Cl$_2$.1.5 H_2O (red-violet prisms) is filtered off, washed with a little ice water and dried in air. (Mol. wt. 391.44; Co: calcd. 15.06, found 14.96; Cl: calcd. 27.17, found 27.03).

The corresponding bromide, *cis*-[Co(*en*)$_2$Cl(pyridine)]Br$_2$ (red prisms), is obtained by double decomposition reaction, too, with 40 – 50 g NaBr in conc. aqueous soln. (Mol. wt. 453.33; Co: calcd. 13.00, found 12.86; Br: calcd. 35.25, found 35.50).

The *cis*-[Co(*en*)$_2$Cl(pyridine)]I$_2$ (red-brown microcryst.) is prepared with 25 – 30 g KI in 100 ml water. (Mol. wt. 547.33; Co: calcd. 10.77, found 10.55; I: calcd. 46.37, found 46.10).

The purities of the complex salts were controlled by determination of the cobalt (complexometrically, after destruction of the samples with 98% sulfuric acid) and halide (potentiometrically with $AgNO_3$ solution) contents.

For assignment of the geometrical configuration, we used the i.r. absorption band of the cobalt-ethylenediamine ring system (The splitting of the CH_2 rocking band in the 870 – 890 cm^{-1} region [9]).

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RÉSUMÉ — On déduit des courbes TG d'$ACl_2 \cdot 1.5\ H_2O$, ABr_2 et AI_2 ("A" = $[Co(en)_2$(pyridine)Cl]) en se servant de la méthode nomographique des auteurs et de celle de Coats-Redfern, les paramètres cinétiques de la réaction de déshydratation d'$ACl_2 \cdot 1.5\ H_2O$ et de la réaction de substitution de la pyridine à l'anion de la sphère externe. On a étudié l'influence du poids du prélèvement et de la vitesse du chauffage. L'analyse statistique des résultats montre que l'énergie d'activation apparente E de la réaction de substitution diminue dans l'ordre Cl > Br > I et que E et les valeurs du "facteur pré-exponentiel" diminuent toutes deux avec l'augmentation du poids du prélèvement et de la vitesse de chauffage. On discute "l'effet de la compensation cinétique".

ZUSAMMENFASSUNG — Kinetische Parameter der Dehydratationsreaktion von $ACl_2 \cdot 1.5H_2O$ und der Substitutionsreaktion von Pyridin für das Anion der äusseren Sphäre wurden aus den TG-Kurven von $ACl_2 \cdot 1.5H_2O$, ABr_2 und AI_2 (A = $[Co(en)_2$(pyridin)Cl] unter Anwendung der Nomogramm-Methode der Autoren sowie der von Coats-Redfern abgeleitet. Der Einfluss des Probengewichts und der Aufheizgeschwindigkeit wurde untersucht. Die statistische Analyse der Ergebnisse zeigte eine Abnahme der scheinbaren Aktivierungsenergie der Substitutionsreaktion in der Reihenfolge Cl > Br > I, sowie die Abnahme von E und des "prä-exponentiellen Faktors" mit zunehmendem Gewicht der Probe und zunehmender Aufheizgeschwindigkeit. Der "kinetische Kompensationseffekt" wird diskutiert.

Резюме — Кинетические параметры реакции дегидратации $ACl_2 \cdot 1.5H_2O$ и реакции замещения пиридина на внешне-сферный анион, были выведены из кривых ТГ комплексов $ACl_2 \cdot 1.5H_2O$, ABr_2 и AI_2 (A = [Co/*en*)$_2$(пиридин)Cl]), используя собственный метод номограмм и метод Коутса – Рэдферна. Изучено влияние веса образца и скорости нагрева. Статистический анализ результатов показал, что кажущаяся энергия активации (E) реакции замещения уменьшается в ряду Cl > Br > I. Значения E и «предэкспоненциального фактора» уменьшаются с увеличением веса образца и скорости нагрева. Обсужден «кинетический компенсационный эффект».