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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA. XXI. DERIVATOGRAPHIC STUDY ON THE THERMAL DECOMPOSITION OF SOME $[Co(en)_2X_2]Y$ AND $[Co(en)_2X(AMINE)]Y_2$ TYPE COMPLEXES

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ABSTRACT

The thermal decomposition of 26 complexes of the type $[Co(en)_2X_2]Y$ and *cis*-$[Co(en)_2(amine)X]Y_2$ (where X is Cl or Br; Y is Cl, Br, I, NCS or NCO; amine is aniline, pyridine, β-picoline or *o*-anisidine, and en is ethylenediamine) has been studied by means of a derivatograph. The correlation between the content of water of crystallization, *cis–trans* isomerism and nature of the external sphere anion is discussed. The first stage of the pyrolysis of *cis*-$[Co(en)_2(amine)X]Y_2$ type complexes is the substitution of the amine ligand for an external sphere anion. From the TG curves, kinetic parameters have been derived for some dehydration and de-amination reactions.

INTRODUCTION

The study of the thermal decomposition of metal–amine complexes of various types has been the subject of many investigations with a wide variety of experimental techniques in the last 2–3 decades. Wendlandt et al. studied the thermal decomposition of some cobalt(III) [1] and chromium(III) [2] amine complexes of the type $[M(NH_3)_6]X_3$, $[M(NH_3)_5X]Y_2$, $[M(NH_3)_4X_2]Y$ by means of TG and DTA measurements. The intermediate pyrolysis products were identified and characterized by IR and UV reflectance spectroscopy and magnetic measurements. The kinetics and mechanism of these processes were also studied and discussed.

The anation and thermal de-aquation reactions of $[M(NH_3)_5(H_2O)]X_3$, $[M(NH_3)_4(H_2O)_2]X_3$ and $[M(NH_3)_3(H_2O)_3]X_3$ were also studied by Wendlandt and Fischer [3] under analogous experimental conditions.

The thermal decomposition of various transition metal complexes with aliphatic diamines, e.g. ethylenediamine, 1,2- and 1,3-propanediamine and its N-substituted products, has also been investigated in this way, e.g. $[Ni(en)_3]X_2$, $[Ni(pn)_3]X_2$ [4], $[Ni(R\text{-}en)_3]X_2$ [5], $[Zn(en)_3]X_2$ [6], $[Cu(en)_3]X_2$, $[Cu(pn)_3]X_2$ [7], $[Pd(en)_2]X_2$ [8].

Pfeiffer [9] and Rollinson and Bailar [9] observed that the $[Cr(en)_3]X_3$ type complexes undergo partial de-amination with the formation of *cis*- or *trans*-$[Cr(en)_2X_2]X$. Wendlandt et al. [10] derived a thermal matrix method which enabled them to obtain some complexes of the type $[Cr(diamine)_2X_2]X$, impossible to synthesize by a wet process. The kinetics of this partial de-amination reaction were also studied in our previous works [11], under isothermal and dynamic temperature conditions.

The ethylenediamine complexes of Co(III) of various types were also studied by means of different thermal analytical methods. Collins et al. [12] and Lazerko et al. [13] studied the thermal decomposition of some $[Co(en)_3]X_3$ type complexes. In some cases, $[Co(en)_2X_2]X$ derivatives appear as decomposition intermediate products; however, the partial de-amination reaction is complicated by redox processes [Co(III)–Co(II)].

Chang and Wendlandt [14] followed the kinetics and mechanism of the thermal anation and de-aquation of the aquo-complexes: $[Co(en)_2(H_2O)_2]X_3$, $[Co(en)_2(H_2O)X]Y_2$ (where X and Y = halide and pseudohalide ion, respectively).

In our previous works a thermogravimetric study has been made on the thermal decomposition of some $[Co(en)_2(amine)X]Y_2$ type complexes. TG curves of the complexes
amine = pyridine, X = Cl, Y = Cl, Br, I [15]
amine = pyridine, X = Br, Y = Br, I [16]
amine = aniline, X = Br, Y = Br [17]
amine = β-picoline, X = Cl, Y = I [17]
have been recorded for 25, 50, 75 and 100 mg samples with heating rates of 5, 10 and 15°C min^{-1}. In all cases the first stage of the thermal decomposition seems to be a substitution reaction of the amine molecule for an external sphere anion Y. The kinetic parameters have been derived from the TG curves for this reaction. The dependence of the apparent kinetic parameters on working conditions has been observed, viz. both increasing sample weight and increasing heating rates led to the decrease of the apparent activation energy E, as well as of the pre-exponential factor Z. The simultaneous variation of E and Z obeyed a linear kinetic compensation law

$$\log Z = aE + b \quad (1)$$

By comparing the mean values of the kinetic parameters obtained for the same compound under different working conditions, one could observe a decrease of E as function of Y in the order Cl, Br > I, and a decrease in the decomposition temperature in the same order.

EXPERIMENTAL

trans-$[Co(en)_2Cl_2]Cl$ was obtained using Werner's method [22], by the air oxidation of the components in aqueous solution.

cis-$[Co(en)_2Cl_2]Cl$ was obtained by six to eight fold evaporation to dryness of the aqueous solution of the acid-free *trans*-$[Co(en)_2Cl_2]Cl$.

trans-$[Co(en)_2Br_2]Br$ forms during the five to six fold evaporation to dryness on a water bath of the *trans*-$[Co(en)_2Cl_2]Cl$ with concentrated HBr solution.

cis-$[Co(en)_2Cl(amine)]X_2$ salts were obtained by Meisenheimer and Kiderlen's method from *trans*-$[Co(en)_2Cl_2]Cl$ and the corresponding amines [23].

The halide and pseudohalide salts of the above-mentioned cations were obtained by means of double decomposition reactions with an excess of 5–20% NaBr, KI, KCNS, KCNO solutions.

The purities of the complex salts were controlled by the determination of the cobalt (complexometrically, after destruction of the samples with concentrated sulphuric acid), halide and pseudohalide (potentiometrically with $AgNO_3$ solution), nitrogen (Dumas's method) contents.

The derivatographical measurements have been performed by means of a derivatograph (MOM, Budapest) in an atmosphere of air, using 200 mg samples in a platinum crucible, and a constant heating rate of 1 K min^{-1}.

RESULTS AND DISCUSSION

In the present work the thermal decomposition of 26 complexes has been studied by means of a derivatograph (MOM, Budapest). The molecular formulae of the 14 $[Co(en)_2X_2]Y$ type and the 12 *cis*-$[Co(en)_2(amine)X]Y_2$ type complexes studied are given below

1. *cis*-$[Co(en)_2Cl_2]Cl \cdot H_2O$
2. *trans*-$[Co(en)_2Cl_2]Cl$
3. *cis*-$[Co(en)_2Cl_2]Br \cdot H_2O$
4. *trans*-$[Co(en)_2Cl_2]Br$
5. *cis*-$[Co(en)_2Cl_2]I$
6. *trans*-$[Co(en)_2Cl_2]I$
7. *cis*-$[Co(en)_2Cl_2]NCS$
8. *trans*-$[Co(en)_2Cl_2]NCS$
9. *cis*-$[Co(en)_2Cl_2]NCO$
10. *trans*-$[Co(en)_2Cl_2]NCO$
11. *trans*-$[Co(en)_2Br_2]Br \cdot H_2O$
12. *trans*-$[Co(en)_2Br_2]I$
13. *trans*-$[Co(en)_2Br_2]NCS$
14. *trans*-$[Co(en)_2Br_2]NCO$
15. *cis*-$[Co(en)_2(an)Cl]Cl_2 \cdot H_2O$
16. *cis*-$[Co(en)_2(an)Cl]I_2$
17. *cis*-$[Co(en)_2(an)Cl](NCS)_2$
18. *cis*-$[Co(en)_2(an)Br]I_2$
19. *cis*-$[Co(en)_2(py)Cl]Br_2$
20. *cis*-$[Co(en)_2(py)Cl]I_2$
21. *cis*-$[Co(en)_2(py)Br]Cl_2 \cdot H_2O$
22. *cis*-$[Co(en)_2(py)Br]Br_2$
23. *cis*-$[Co(en)_2(py)Br]I_2$
24. *cis*-$[Co(en)_2(pic)Br]Br_2 \cdot 2\,H_2O$
25. *cis*-$[Co(en)_2(pic)Br]I_2$
26. *cis*-$[Co(en)_2(anis)Cl]I_2$

(en = ethylenediamine, an = aniline, py = pyridine, pic = β-picoline, anis = *o*-anisidine).

As seen, six of the complexes also contain water of crystallization. It is worth mentioning that five of them are *cis*-isomers and only one is a *trans*-isomer. The external sphere anions of all crystal hydrates are Cl^- or Br^-. This suggests that the water of crystallization is linked to the external sphere anion. All *cis*-chlorides are crystal hydrates, which is consistent with the above hypothesis, since the intensity of the electrostatic field generated by the external sphere anion is higher in the case of Cl^- ions. Among the *cis*-bromides, about half contain water of crystallization, but none of the iodides, thiocyanates or cyanates does.

Thermal decomposition of the $[Co(en)_2X_2]Y$ *type complexes*

The TG and DTA curves recorded at a constant heating rate of 1°C min^{-1} up to 350°C are given for some $[Co(en)_2X_2]Y$ type complexes in Fig. 1. The formation of a relatively stable intermediate is obvious only in the case of the crystal hydrates, viz. a weight loss stop is observed on the TG curves corresponding to the formation of the anhydrous complex. The thermal decomposition of the complex cation occurs with the formation of no well-defined intermediate and it might imply the superposition of several chemical reactions. At the beginning of the thermal decomposition a characteristic endothermic peak appears on the DTA curves of each complex. Its position is given in Table 1.

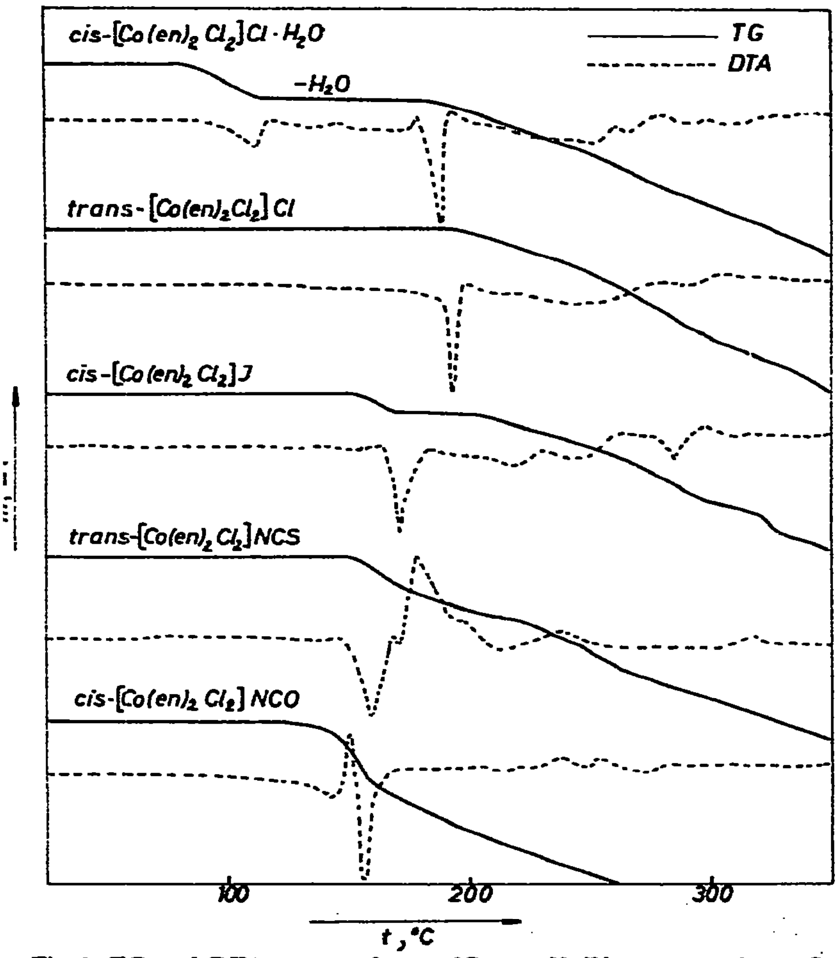

Fig. 1. TG and DTA curves of some $[Co(en)_2X_2]Y$ type complexes. Sample weight=200 mg; heating rate=1°C min^{-1}. en=Ethylenediamine.

TABLE 1

Position of the endothermic peak (in °C) on the DTA curves of $[Co(en)_2X_2]Y$ type complexes

Y	X=Cl		X=Br
	cis	*trans*	*trans*
Cl	182	192	
Br	178	181	185
I	174	176	184
NCS	168	162	182
NCO	152	168	160

These data suggest that the first stage of the thermal decomposition involves the partial substitution of the ethylenediamine for the external sphere anion. The shift of the endothermic peak temperature towards lower temperatures in the order Cl > Br > I > NCS, NCO is in agreement with this presumption, since the Co–ligand bond strength increases in the same order, taking into account the π-bond formation possibilities with the NCS^- and NCO^- ions. Meanwhile, the *trans*-isomers seem to be more stable than the *cis*-isomers. Concerning the influence of the X ligand, generally, the bromo-complexes show a higher stability as compared to the chloro-complexes.

Further stages of the thermal decomposition are rather obscure. Frequently, at 300–350°C the weight loss already exceeds the value corresponding to the formation of CoX_2Y and no weight loss stop or inflexion appears. Thus, the elimination of the halogens and pseudo halogens, too, is obvious. The participation of the atmospheric oxygen in the pyrolysis processes is marked by exothermic DTA peaks in the case of the NCS and NCO salts.

Thermal decomposition of cis-$[Co(en)_2(amine)X]Y_2$ type complexes

The TG and DTA curves recorded at a constant heating rate of 1°C min^{-1} up to 200°C are given for some $[Co(en)_2(amine)X]Y_2$ type complexes in Fig. 2. In some cases the elimination of the water of crystallization can be observed as the first stage of the thermal decomposition, and a relatively well-defined weight loss stop appears, corresponding to the anhydrous complex. The decomposition of the anhydrous complex leads to the formation of a $[Co(en)_2XY]Y$ type intermediate, as observed in our earlier papers [15–17].

The observed weight loss stop corresponds almost exactly to the formation of this intermediate (as seen from Table 2), containing the number of amine molecules eliminated up to the weight loss stop, as well as the corresponding temperature. These data are consistent with the substitution reaction

$$[Co(en)_2(amine)X]^{2+} + Y^- \rightarrow [Co(en)_2XY]^+ + amine \qquad (2)$$

The only exception is $[Co(en)_2(anis)Cl]I_2$, showing an anomalous behaviour also in other respects. Thus, its thermal decomposition begins almost at room temperature,

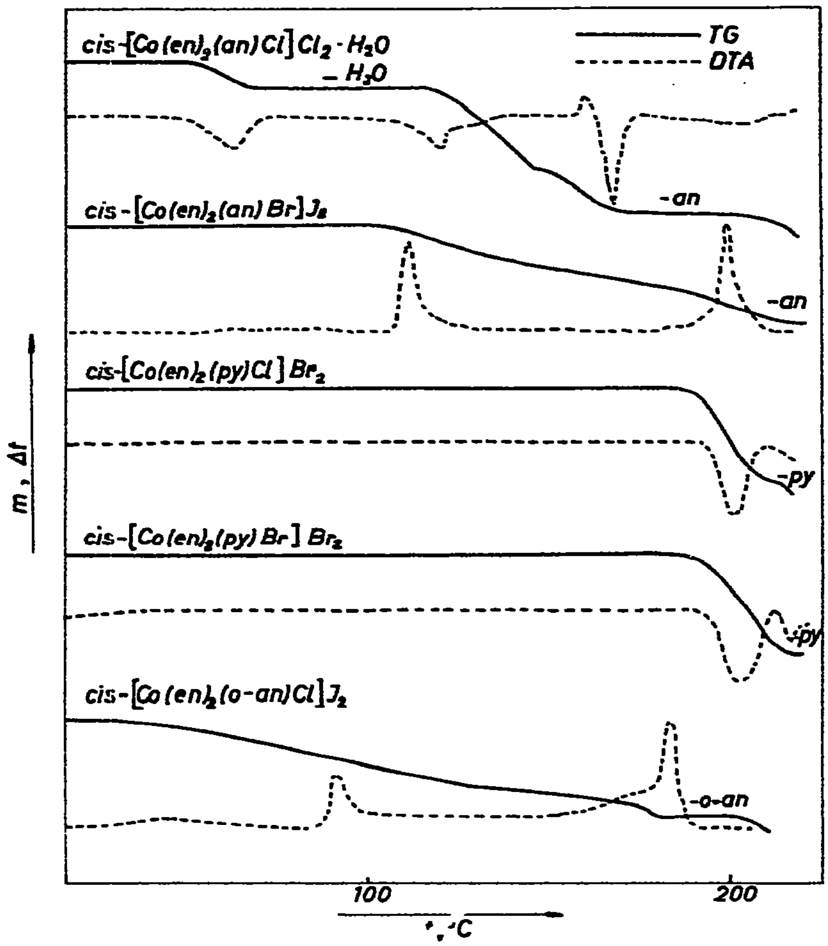

Fig. 2. TG and DTA curves of some $[Co(en)_2(amine)X]Y_2$ type complexes. Sample weight=200 mg: heating rate 1°C min^{-1}. en=Ethylenediamine, an=aniline, py=pyridine, *o*-an=*o*-anisidine.

marking the instability of the complex ion. This may be due to a steric hindrance because of the *ortho*-position of the OCH_3 group of the anisidine molecule. The only weight loss stop is observed at 185°C, corresponding to the elimination of 85% of the liberated amine. Since the boiling point of the *o*-anisidine is much higher than this temperature (225°C), one can presume the substitution reaction (2) to occur, but a part of the liberated *o*-anisidine to be retained in the sample.

A similar phenomenon is observed with *cis*-$[Co(en)_2(an)Cl]Cl_2$, where the elimination of the aniline occurs in two stages. On the TG curve an inflexion point appears after the loss of 0.67 aniline molecule, corresponding to about 143°C. One can presume the last part of the aniline to be vaporized only at higher temperatures, marked by a clear endothermic peak on the DTA curve at 170°C. Since the boiling point of aniline is 184.4°C and a low heating rate of 1°C min^{-1} was used, the position of this endothermic peak is consistent with the above hypothesis.

The substitution reaction (2) seems to be a unitary process only if the amine is pyridine or *β*-picoline (the boiling points are 115.5 and 143.5°C, respectively) and

TABLE 2

Formation of the $[Co(en)_2XY]Y$ type intermediate

Complex	No. of amine molecules lost	t_1 (°C)	Complexes	No. amine molecules lost	t_1 (°C)
$[Co(en)_2(an)Cl]Cl_2 \cdot H_2O$	1.00	170	$[Co(en)_2(py)Br]Cl_2$	0.93	205
$[Co(en)_2(an)Cl]I_2$	1.00	175	$[Co(en)_2(py)Br]Br_2$	1.04	215
$[Co(en)_2(an)Cl](NCS)_2$	0.98	190	$[Co(en)_2(py)Br]I_2$	1.01	170
$[Co(en)_2(an)Br]I_2$	1.01	200	$[Co(en)_2(pic)Br]Br_2$	0.99	198
$[Co(en)_2(py)Cl]Br_2$	0.97	207	$[Co(en)_2(pic)Br]I_2$	1.02	192
$[Co(en)_2(py)Cl]I_2$	0.98	190	$[Co(en)_2(anis)Cl]I_2$	0.84	185

Y^- is Cl^- or Br^-. In all these cases only endothermic peaks are observed on the DTA curves. In all other cases the above reaction occurs at least in two stages and exothermic effects are also observed. If the external sphere anion is I^- the thermal decomposition begins at lower temperatures and generally an exothermic peak appears at the beginning of the reaction and another one at higher temperatures. The first peak may be related to the substitution reaction (2) which becomes exothermic presumably due to the higher Co–I bond strength as compared to the Co–Cl and Co–Br bonds. The second exothermic peak may show some redox processes. The thermal decomposition of the thiocyanates is more complex and begins at even lower temperatures than that of the iodides, and the superposition of several exothermic processes is observed, implying also oxidation reactions with the participation of the atmospheric oxygen.

Derivation of kinetic parameters

The shape of the TG curves allows derivation of kinetic parameters only for the loss of the water of crystallization of the six crystal hydrates and for reaction (2) of the four chlorides and bromides of pyridine or β-picoline containing complexes of the *cis*-$[Co(en)_2(amine)X]Y_2$ type. In order to derive kinetic parameters, the nomogram method [15,18] has been used. All these dehydration and de-amination processes are marked by a well-defined endothermic peak on the DTA curve. Its position is given in Table 3, which also contains the characteristic temperatures $t_{0.1}$, $t_{0.5}$, $t_{0.9}$ and t_m; t_α is the temperature in °C at which the conversion attains the values $\alpha = 0.1$, 0.5 and 0.9, respectively, t_m is the maximum decomposition rate temperature (DTG peak temperature).

Table 4 contains the shape and position parameters ∇, Δ and τ defined in ref. 18, as well as the reduced position parameter τ^* and the kinetic parameters n (apparent reaction order), E (apparent activation energy) and Z (apparent pre-exponention factor expressed in s^{-1}) derived for the same dehydration and de-amination reactions. As seen, the apparent activation energies of the dehydration reactions are lower than the E values of the de-amination reactions, the latter occurring at higher

TABLE 3

Endothermic DTA peak temperatures (°C) and characteristic TG temperatures (°C) of the dehydration and de-amination reactions

Reaction	Endothermic peak temperature	Characteristic temperatures			
		$t_{0.1}$	$t_{0.5}$	$t_{0.9}$	t_m
Dehydration of					
cis-$[Co(en)_2Cl_2]Cl \cdot H_2O$	114	91	106	114	112
cis-$[Co(en)_2Cl_2]Br \cdot H_2O$	108	88	99	103	104
trans-$[Co(en)_2Br_2]Br \cdot H_2O$	78	68	73	81	76
cis-$[Co(en)_2(an)Cl]Cl_2 \cdot H_2O$	60	46	57	67	60
cis-$[Co(en)_2(py)Br]Cl_2 \cdot H_2O$	105	48	92	130	105
cis-$[Co(en)_2(pic)Br]Br_2 \cdot H_2O$	93	78	88	96	93
De-amination of					
cis-$[Co(en)_2(py)Cl]Br_2$	200	192	198	202	194
cis-$[Co(en)_2(py)Br]Cl_2$	192	187	194	201	192
cis-$[Co(en)_2(py)Br]Br_2$	202	195	202	210	201
cis-$[Co(en)_2(pic)Br]Br_2$	178	163	176	191	177

TABLE 4

Shape and position parameters of the TG curves and kinetic parameters derived for the dehydration and de-amination reactions

Reaction	∇	Δ	τ	τ^*	n	E (kJ $mole^{-1}$)	log Z
Dehydration of							
cis-$[Co(en)_2Cl_2]Cl \cdot H_2O$	0.273	109	2.747	2.591	0.04	117	13.1
cis-$[Co(en)_2Cl_2]Br \cdot H_2O$	0.254	82	2.770	2.651	−0.10	154	18.6
trans-$[Co(en)_2Br_2]Br \cdot H_2O$	0.602	43	2.933	2.899	3.38	510	73.9
cis-$[Co(en)_2(an)Cl]Cl_2 \cdot H_2O$	0.459	105	3.135	3.021	1.61	157	22.4
cis-$[Co(en)_2(py)Br]Cl_2 \cdot H_2O$	0.412	375	3.115	2.672	1.18	37	1.9
cis-$[Co(en)_2(pic)Br]Br_2 \cdot 2\ H_2O$	0.432	79	2.849	2.760	1.35	202	26.6
De-amination of							
cis-$[Co(en)_2(py)Cl]Br_2$	0.400	27	2.150	2.117	1.06	574	61.1
cis-$[Co(en)_2(py)Br]Cl_2$	0.484	33	2.174	2.140	1.87	530	56.6
cis-$[Co(en)_2(py)Br]Br_2$	0.522	32	2.137	2.106	2.30	584	61.5
cis-$[Co(en)_2(pic)Br]Br_2$	0.518	67	2.294	2.229	2.25	272	29.2

temperatures than the former. Generally, the activation energies are higher than obtained for analogous reactions in our earlier works by using higher heating rates. Thus, for the dehydration of *cis*-$[Co(en)_2(py)Cl]Cl_2 \cdot 1.5\ H_2O$ $E = 105$ kJ $mole^{-1}$ [15], for the de-amination of *cis*-$[Co(en)_2(py)Cl]Br_2$ $E = 373$ kJ $mole^{-1}$ [15], and for *cis*-$[Co(en)_2(py)Br]Br_2$, $E = 352$ kJ $mole^{-1}$ [16] values have been obtained. This is in agreement with the observed influence of heating rate upon the apparent kinetic parameters.

All E and log Z values vary in parallel and the graphical plot of log Z vs. E gave

TABLE 5

Kinetic compensation parameters derived from data presented in Table 4

Reaction	a (mole kJ^{-1})	b	R	a' (mole kJ^{-1})
Dehydration	0.152	−3.734	0.998	0.145
De-amination	0.105	0.65	0.999	0.112

two straight lines, one for the dehydration reactions, the other for the de-amination ones, showing the validity of the linear kinetic compensation law (1). The kinetic compensation parameters a and b derived by means of the least squares method, as well as Jaffé's correlation coefficient R [19], are given in Table 5. As seen, the R values indicate a very good linearity. Table 5 also contains the parameter

$$a' = \frac{\log e}{RT_c}$$

which corresponds to the slope of the log Z vs. E straight line, according to Garn's hypothesis [20]. In this formula T_c is a standard decomposition temperature. Values given in Table 5 have been calculated by taking

$$T_c = \frac{1000}{\bar{\tau}^*}$$

where $\bar{\tau}^*$ is the mean value of the reduced position parameters τ^* given in Table 4.

Obviously, a and a' values are rather close to each other, which seems to support Garn's hypothesis. It is worth mentioning that the a values obtained in our earlier works for the de-amination of $[Co(en)_2(py)X]Y_2$ type complexes fall between 0.104 and 0.108 [15–17]. For dehydration reactions, a values between 0.147 and 0.164 have been obtained earlier [11,15,21]. Thus, the values derived in the present work are perfectly consistent with those reported earlier.

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