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LINEAR RELATIONS OF ACTIVATION ENERGY IN NON-ISOTHERMAL KINETICS

D. Fatu

Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest,
Blv. Elisabeta 4–12, Bucharest, 70346 Romania

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Abstract

The object of this work is the quantitative explanation of linear correlation between activation energy (E), initial decomposition temperature (T_i) and ionic potential (V_i), observed for thermal degradation of some complexes of transitional metals.

The proposed model allowed the evaluation of characteristic parameter proportional to the activation free enthalpy and also the variation of effective electrical charge (ΔQ^*) of ligand, in the formation process of the activated complex.

These results are satisfactory, taking into account that we utilized many simple hypotheses for deduction of Arrhenius equation.

Keywords: complexes of Co, Ni, Mn, Cu, non-isothermal kinetics

Introduction

In previous works [1–3], concerning the thermal behavior of coordination compounds, correlation between activation energy, initial decomposition temperature and some properties of central ions were reported.

This paper aims at giving some quantitative background for such a correlation. In literature [4, 5], a special attention has been paid to the compensation effect in non-isothermal kinetics which corresponds to the linear dependence between the logarithm of the pre-exponential factor *vs*. activation energy.

Theoretical part

Correlation between activation energy (E) and initial decomposition temperature (T_i)

The initial reaction rate (v_i) and the initial temperature T_i are expressed by the following equations:

$$v_i = \frac{d\alpha_i}{dt} = A e^{-E/RT_i} f(\alpha_i) \qquad (1)$$

$$T=T_i;\ \alpha=\alpha_i=0.01;\ v=v_i \tag{2}$$

where α stands for degree of conversion; t – time; A – pre-exponential factor; E – activation energy; R – gas constant; $f(\alpha)$ – conversion function.

If the activation energy (evaluated by using a differential method) depends on α in the initial period of the thermal decomposition is necessary to utilize in Eq. (1) the value $E(\alpha_i)$. By convention, T_i was considered as temperature defined from condition (2). In order to take into consideration the zero point activation energy, the parameter E must be substituted in Eq. (1) by $E+\Delta E_0$. By taking the logarithms one obtains:

$$E=CT_i \quad \Delta E_0 \tag{3}$$

Here

$$C=R\ln\frac{Af(\alpha_i)}{v_i} \tag{4}$$

and ΔE_0 represents the zero-point activation energy per mole [6].

For a set of related reactions the expression C may be considered quasi-constant. Under such conditions the Eq. (3) indicates a linear correlation of E and T_i.

Correlation between the activation energy and the ionic potential of the central coordinated metal

In order to obtain the relation between E and ionic potential (V_i), the rate constant (k_r) after Eyring and Arrhenius, is used in the forms:

$$\ln k_r=\ln\frac{\chi kT}{h}-\frac{\Delta G^*}{RT} \tag{5}$$

$$\ln k_r=\ln A-\frac{E}{RT} \tag{6}$$

where χ, k and h represent transmission coefficient, Boltzmann, respectively Planck constants. Gibbs activation enthalpy ΔG^* is composed of a non-electrostatic (n) and electrostatic (e) term. Under such conditions from (5) and (6) one obtains:

$$E=RT\ln\frac{Ah}{\chi kT}+\Delta G_n^*-\Delta Q^*V_i \tag{7}$$

The product of the ligand effective electrical charge variation (ΔQ^*), in the formation process of the activated complex and ionic potential represents the electrostatic term.

The electric interaction energy between the central ion and the ligand depends on the ionic potential and ligand properties (the dipole moment and polarizability coefficient). These are difficult to be estimated especially for high volume ligands. For this reason, the molar interaction energy, W (J mol^{-1}), was approximated by: $W=QV_i$ where Q (C mol^{-1}) has the meaning of an equivalent electrical charge, specific to the ligand.

By using the notations:

$$\rho = RT_i \ln\frac{Ah}{\chi kT_i} + \Delta G_n^* \approx \Delta G_n^* = \text{const.} \tag{8}$$

$$\lambda = -\Delta Q^* \tag{9}$$

the relation (7) takes the following form:

$$E = \rho + \lambda V_i \tag{10}$$

The parameter ρ (kJ mol^{-1}) is related to the type of decomposition reaction and λ (kC mol^{-1}) characterizes the ligand, in the electrostatic interaction with the central ion. The central ion potential is calculated using the expression:

$$V_i = \frac{Z_i e}{4\pi\varepsilon_0 R_i} \tag{11}$$

where Z_i and R_i represent the electrical charge and the central ion radius, e – elemental charge and ε_0 – electrical permittivity of vacuum.

In the case of thermal decomposition of a complex group containing the same ligand but different central ions, the parameters ρ and λ may be considered quasi-constants and according to the Eq. (10) the correlation E *vs.* V_i will be linear.

Experimental

The heating curves were recorded by means of a C-Derivatograph (MOM, Budapest) and a thermal analysis device DuPont 2000, in air and in nitrogen atmosphere, using heating rates changing from 2 to 10 K min^{-1}.

Results and discussions

In our laboratory, qualitative correlations of E, T_i and V_i were put in evidence for the first time in the non-isothermal study of pyridine complexes of Co, Ni, Mn chlorides [1]. Later such correlations were reported for the complexes of Schiff bases [2] and glyoxal-bis-4-methoxy-*o*-aminophenol-2 with some transitional ions [3]. In this section we try to verify if the experimental data may be described by Eqs (3) and (10), proposed in this framework.

Decomposition of pyridine complexes with Co, Ni, Mn chlorides

The data obtained for the first step of decomposition, described by the stoichiometric equation:

$$[MPy_4]Cl_2(s) \rightarrow [MPy_2]Cl_2(s) + 2Py(g) \tag{I}$$

where M= Co(II), Ni(II), Mn(II), are presented in Table 1.

Table 1 Data for pyridine complexes

Complex	T_i/K	E/±1.4 kJ mol^{-1}	V_i/V
$[MnPy_4]Cl_2$	297	66.8	31.6
$[CoPy_4]Cl_2$	324	79.4	40.0
$[NiPy_4]Cl_2$	355	87.7	41.7

The activation energy for low conversion values was evaluated using the equation:

$$\ln\frac{d\alpha}{dt}=\ln A-\frac{E}{RT} \tag{12}$$

Equation (12) is the approximated form of the Eq. (1) for $f(\alpha)=(1-\alpha)^n$ and $\alpha<<1$, because for $\alpha<<1$ the value of $f(\alpha)\cong 1$. The plot of V_i *vs.* T_1, presented in Fig. 1, shows a linear dependence, according to Eq. (3). From the linear regression parameters, the data indicated in Table 2 were obtained.

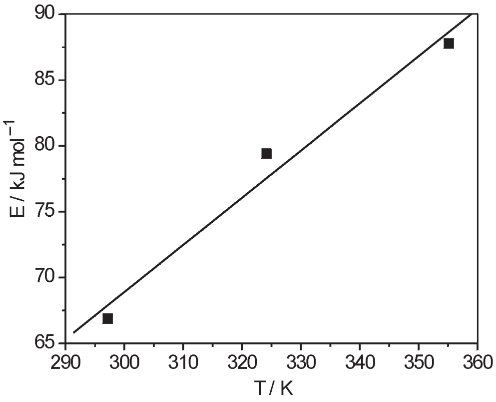


Fig. 1 Linear regression corresponding to Eq. (3) for pyridine complexes

Table 2 Parameters of Eq. (3) corresponding to pyridine complex

C/kJ mol^{-1}K^{-1}	ΔE_0/kJ mol^{-1}	r
0.358	38.5	0.9881

C – slope; ΔE_0 – variation of residual (zero-point) energy; r – correlation coefficient

To verify Eq. (10), the E *vs.* V_i data from Table 1 were plotted in Fig. 2, and the corresponding parameters are shown in Table 3.

Table 3 Parameters of Eq. (10) corresponding to pyridine complex

ρ/kJ mol^{-1}	λ/kC mol^{-1}	r
6.55	1.89	0.96972

λ – variation of equivalent charge; ρ – Gibbs activation enthalpy; r – correlation coefficient

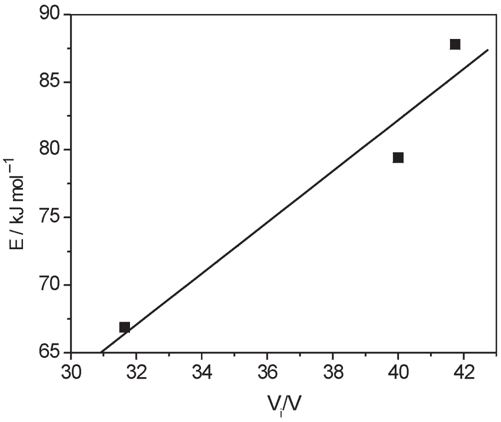
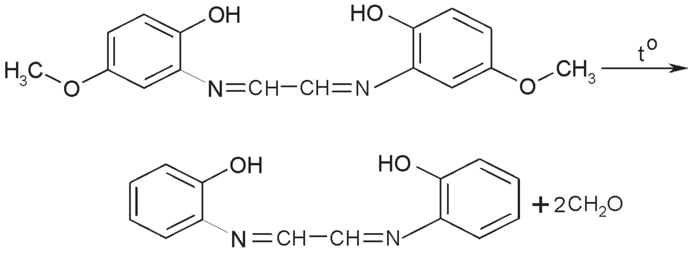


Fig. 2 Linear regression corresponding to Eq. (10) for pyridine complexes

Decomposition of glyoxal-bis-4-methoxy-o-aminophenol-2 polynuclear complex with Mn(II), Co(II), Ni(II) and Cu(II)

The composition of the four polynuclear complexes [3] corresponds to the general formula $[Mn]_n$, where *M* stands for the transitional ion and *L*, for the ligand (glyoxal-bis-4-methoxy-*o*-aminophenol-2). The first step of decomposition consists in the degradation of methoxy groups, evolving formic aldehyde as it is presented below:



Activation energy values, calculated by the same method, for the decomposition of this polynuclear complexes group, increase proportionally to the initial temperature of decomposition and the ionic potential, according to the Eqs (3) and (10) (Figs 3 and 4).

Parameters for the regression straight lines corresponding of Eqs (3) and (10) are indicated in Tables 4 and 5.

Table 4 Parameters of Eq. (3) corresponding to polynuclear complex

C/kJ mol^{-1} K^{-1}	ΔE_0/kJ mol^{-1}	*r*
0.737	228.7	0.9824

C – slope; ΔE_0 – variation of residual zero-point energy; *r* – correlation coefficient

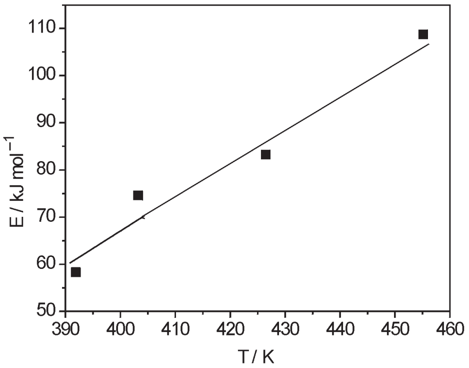


Fig. 3 Linear regression corresponding to Eq. (3) for the polynuclear complexes

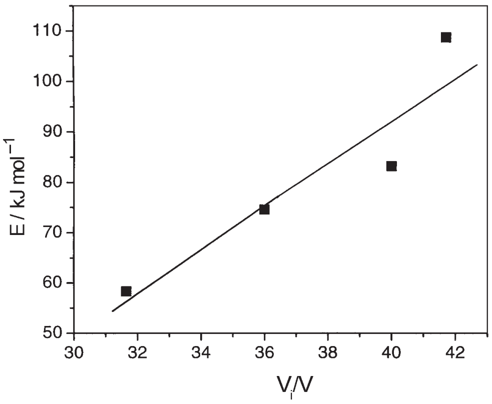


Fig. 4 Linear regression corresponding to Eq. (10) for the polynuclear complexes

Table 5 Parameters of Eq. (10) corresponding to polynuclear complex

ρ/kJ mol^{-1}	λ/kC mol^{-1}	*r*
82.4	4.3	0.9359

λ – variation of equivalent charge; ρ – Gibbs activation enthalpy; *r* – correlation coefficient

Conclusions

- A theoretical model was elaborated to explain the linear correlation of activation energy, initial temperature of decomposition and ionic potential, observed for the non-isothermal degradation of pyridine and glyoxal-bis-4-methoxy-*o*-aminophenol-2 complex with Co(II), Ni(II), Mn(II) and Cu(II).
- For simplicity the electrostatic interaction energy in the complex molecule was approximated by the product of ionic potential and an ‘equivalent charge’ of the ligand.

- Parameters C, ΔE_0, ρ and λ, from the proposed linear equations are characteristic of the decomposition reaction and of the ligand. The values of these parameters are higher for this higher volume ligand (glyoxal-bis-4-methoxy-*o*-aminophenol-2).

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