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A COMPARATIVE STUDY OF THE THERMAL STABILITY OF COORDINATION COMPOUNDS BY THERMOANALYTICAL METHODS

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The informative capacity of thermal analysis in the evaluation of the thermal stability of coordination compounds involving the evolution of volatile ligands is discussed. The temperature of decomposition under quasi-equilibrium conditions (Q-derivatograph, quasi-isobaric, quasi-isothermal operation) is suitable for characterizing the thermodynamic stability of compounds. The initial temperature of decomposition at linear heating indicates the reaching of a defined value of the rate constant (depending on the sensitivity of the sensing device of the instrument and on experimental conditions). The temperature sequence of increasing thermal stability may not coincide with the sequence of increasing activation energy values, since in the majority of cases it demands on the value of activation enthropy.

Many thermal reactions of coordination compounds involving the evolution of volatile ligands may be regarded as heterogeneous ligand exchange processes. It is therefore of interest to compare thermodynamic and kinetic stabilities for series of coordination compounds in similar-type. The sequences may be obtained if the equilibrium constants and the rate constants of the reactions in question are known at some standard temperature. It is difficult, however, to choose the standard temperature. Known sequences of stability for reactions of coordination compounds in solution are based, for instance, on data of stability constants determined at 25°, and the total temperature range of the experiment does not exceed 0 to 100° (at atmospheric pressure). The majority of crystalline coordination compounds are being synthetized at ambient temperature, and are rather stable at 25° both kinetically and thermodynamically. The temperature range of interest for studying solid-phase transformations is much broader.

Since thermal analysis is a traditional method for studying coordination compounds efforts have been made for a long time past to obtain qualitative sequences of their thermal stability indirectly from thermoanalytical data without determining the numerical values of the equilibrium constants and rate constants (at standard temperature).

The sequences of the thermodynamic stability of isostructural compounds in similar-type can be obtained using the Q-derivatograph [1–2]. The particular features of the experimental method are as follows: dynamic heating of the sample at a determined rate takes place only up to the start of weight loss. As soon as weight loss begins a special system takes over the control of oven heating, the objective being a constant and small rate of weight loss (< 1 mg/min). The "quasi-equilibrium" being established for reversible reactions leads to a stabilization of the temperature almost up to the end of the process (quasi-isothermal operation) [3]. It is known that the evolution rate of the gaseous reaction product varies with different shapes of the crucible. The experiment can thus be carried out at different gas pressures by using polyplate crucible ($p \approx 0.01$ atm), standard open crucible ($p \approx 0.05$ atm) covered crucible ($p \approx 0.2$ atm) and labyrinth crucible ($p \approx 1$ atm) [3, 4]. The quasi-isothermal temperature of analysis in the labyrinth crucible (where gas exit is hindered) appears characteristic or the thermodynamic stability of the compouind since at this temperature, funder conditions close to the equilibrium, two sold phases are present at a practically constant partial pressure of the gas being evolved ($p_{\text{gas}} \approx 1$ atm).

This temperature does not depend on the mass of the sample and on the dispersity of the substance and appears characteristic. The sequence of the thermal stability of coordination compounds based on these temperatures appears to be the sequence of their thermodynamic stability in similar-type reactions.

The next question is how to evaluate kinetic stability and establish an analogous (qualitative) sequence.

The characteristics of the dynamic thermoanalytical experiment with linear heating indicate that the starting temperature of decomposition (determined from the deviation of the DTA, DTG, TG or evolved gas curves from the zero line) corresponds to that minimum rate of analysis which can be recorded by the sensing device of the instrument used. In general, the total temperature range of reaction will shift towards lower temperatures when sample mass is reduced, thickness of sample layer is reduced, the size of the particles of the substance is reduced, the pressure of the gaseous reaction product is reduced, and linear heating rate is reduced. In this case, it is reasonable to choose conditions at which the temperature of the thermal investigation will be minimum vacuum: or the inert gas flow through the sample. The initial temperature of decomposition for series of compounds are the temperatures which indicate the reaching of the equal process rate is assumed to be controlled by the chemical reaction on the phase boundary (of spherical symmetry), then

$$\mathrm{d}\alpha/\mathrm{d}t = k(1 - \alpha)^{2/3}$$

(α is conversion).

Obviously, if the sensing device is sufficiently sensitive, one can have, in the starting point, $\alpha_0 < 0.001$. Then the value of the term $(1 - \alpha_0)^{2/3}$ will be closely similar for all compounds of the series, and it may be assumed that the rate constants of the studied processes will also be equal. In this case, the temperature sequence of thermal stability will be the sequence of temperatures at which equal rate constants (though highly critical to the experimental conditions) will be reached.

We checked this assumption of the equality of rate constants at the starting temperatures of decomposition by experimental data: for the dehydration re-

Table 1

Kinetic parameters of EDTA chelate dehydration and clathrate analysis (equation for the motion of the phase boundary)

EDTA chelates	E_a	lg A	t_0, °C	—lg k	ΔG^* kcal/mol
$CaMnL \cdot 3H_2O$	33.6	14.0	119	4.4	31.8
$CaCoL \cdot 5H_2O$	28.8	15.5	80	2.1	24.5
$CaNiL \cdot 4H_2O$	25.3	13.4	36	4.2	24.5
$CaCuL \cdot 5H_2O$	12.6	4.7	21	4.5	23.5
$CaZnL \cdot 5H_2O$	37.8	21.7	32	5.0	25.4
$CaCdL \cdot 2H_2O$	29.0	12.1	109	4.2	26.0
$Ca_2L \cdot 7H_2O$	30.8	17.7	19	3.7	24.2
Clathrates					
$C_8H_{18} \cdot 6.7U$	32.1	20.5	23	3.0	20.8
$C_9H_{20} \cdot 7.45U$	38.0	21.8	30	5.1	25.2
$C_{10}H_{22} \cdot 8.06U$	31.0	17.0	31	4.9	24.7
$C_{11}H_{24} \cdot 8.80U$	37.1	20.2	50	4.5	25.6
$C_{12}H_{26} \cdot 9.42U$	29.0	15.0	53	4.1	25.2
$CCl_4 \cdot 3TU$	35.0	21.1	20	4.9	23.9
$C_6H_{12} \cdot 3TU$	32.0	18.8	20	4.6	24.0

L^{4-} = EDTA anion U = urea TU = thiourea

action of EDTA chelates and for the decomposition of urea and thiourea clathrates (Table 1). The kinetic curves studied under non-isothermal conditions were those of gas evolution obtained by using a gas-flowing reactor [5]. The mass of the sample was 5 to 10 mg, helium flow rate through the sample 60 to 120 cm^3/min the sensing device a conductometric detector.

The kinetic parameters of the processes (E_a, A) were determined by the integral method using the TA I B program for the Minsk-32 computer [6]. In all cases, the kinetics of the process were described by the equation for the motion of the phase boundary (spherical or cylindrical symmetry). At the temperatures t_0, the values of the rate constants k and the free activation energies ΔG^* were calculated.

Among 14 studied reactions, for 11 reactions the rate constant at the temperature where decomposition starts has a value between $10^{-4.2}$ and $10^{-5.1}$ s^{-1}. Apparently the minimum rate of decomposition recorded by the conductometric detector applied corresponds to the reaching of the rate constant $k \approx 10^{-4.6}$. At the temperature where decomposition starts, the value of the free activation energy also proved constant: for 12 reactions out of 14, the value was found to be $\Delta G^* = 24.8 \pm 1.3$ kcal/mole. (The deviation of the values does not exceed the experimental error for $E_a \pm 10\%$).

The dehydration of the EDTA chelates $MgML \cdot nH_2O$ had earlier been studied by DTA using the thermoanalyser manufactured by Netzsch [6]. In this series of experiments, owing to different experimental conditions and the differing sensitivity of the detector, the rate constant found was $k \approx 10^{-5.0}\,s^{-1}$.

Thus, the temperature sequences of thermal stability obtained under standard conditions at a linear heating rate prove to be realistic sequences of the temperatures at which equal rate constants of the processes are reached.

It is interesting to notice that in some cases the increase in the "thermal stability" within the series is accompanied by a decrease of the activation energy (cf. the series of clathrates with even-numbered paraffins: $C_8H_{18} \cdot 6.7\,U$, $C_{10}H_{22} \cdot 8.06U$, $C_{12}H_{26} \cdot 9.42U$).

An analysis of the function $\ln k$ *vs.* $1/T$ demonstrates that within a series of compounds, three variants of relationships between kinetic parameters are possible:

(i) $t_1 > t_3 > t_2$
$E_1 = E_3 = E_2$
$A_1 < A_2 < A_3$ (Fig. 1a)

(ii) $t_1 > t_3 > t_2$
$E_1 < E_3 < E_2$
$A_1 < A_2 < A_3$ (Fig. 1b)

(iii) $t_1 > t_3 > t_2$
$E_1 > E_2 > E_3$

The relationship between A_1, A_2 and A_3 is indeterminate, $A_1 < A_2 < A_3$ can also occur (Fig. 1c).

For the series (i) and (ii), and in some cases also for series (iii), the increase in the initial temperatures of decomposition is reverse to that of the pre-exponential factor A_i: the increase in the thermal stability is adequate to the decrease in the activation enthropy of the analysis. The so-called "thermal stability" is controlled in most cases by the probability of the formation of an intermediate state and by the probability of its appropriate geometry to be converted into the

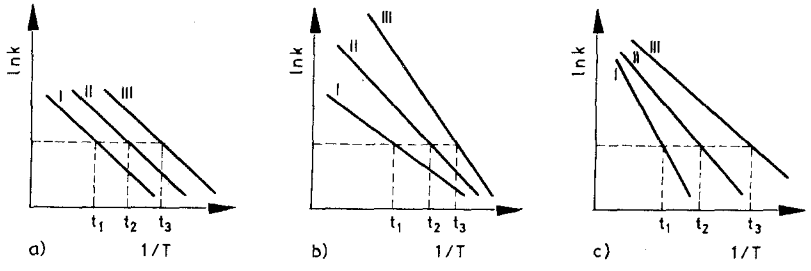

Fig. 1. Three possible variants of relationship between kinetic parameters in the sequence of thermal stability: 1a: $t_1 > t_2 > t_3$, $E_1 = E_2 = E_3$, $A_1 < A_2 < A_3$; 1b: $t_1 > t_2 > t_3$, $E_1 < E_2 < E_3$, $A_1 < A_2 < A_3$; 1c: $t_1 > t_2 > t_3$, $E_1 > E_2 > E_3$. Relationship between A_1, A_2, A_3: indeterminate ($A_1 < A_2 < A_3$ is also possible)

molecules of the product, and not by the energetic characteristics of the metal-ligand bond to be split.

To establish correct macrokinetics of the experiment, certain requirements must be met. Let us list some of them. The kinetic characteristics of the process, not impeded by the reverse reaction, must be obtained under the conditions of "limit vacuum" [7] (or in inert gas flow). The particle size range of the sample should be $d_{max}/d_{min} < 6$ [9] (however, a too fine fraction may lead to a diffuse course of the process [7]), no temperature gradient should be present in the sample (the dimensionless criteria are as follows: temperature increase rate $\Omega < 0.01$ $Bi < 1$ [10]).

If a kinetic meaning is attributed to the temperature at which decomposition begins (equality of the rate constants of the chemical reaction), all these recommendations are imperative at the determination of this temperature too.

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Résumé — L'aptitude de l'analyse thermique à servir de source de données pour l'évaluation de la stabilité thermique des composés de coordination lors des réactions de décomposition mettant en jeu l'élimination de ligands volatils est discutée. En conditions de quasi-équilibre (Derivatograph-Q, opérations quasi-isobares, quasi-isothermes) la température de la décomposition thermique peut être utilisée pour caractériser la stabilité thermodynamique des composés. La température du début de la décomposition en chauffage linéaire indique l'obtention d'une valeur définie de la constante de vitesse (qui dépend de la sensibilité du dispositif détecteur de l'appareil et des conditions expérimentales). L'ordre de succession des températures définissant l'augmentation de la stabilité thermique peut ne pas coincider avec celui des valeurs de l'énergie d'activation, puisque dans la majorité des cas il dépend de la valeur de l'entropie d'activation.

ZUSAMMENFASSUNG — Die informative Kapazität der Thermoanalyse bei der Bewertung der thermischen Stabilität von Koordinationsverbindungen in Thermolysevorgängen unter Entwicklung flüchtiger Liganden wird vorgestellt. Die Temperatur der Thermolyse unter Quasi-Gleichgewichtsbedingungen (Q-Derivatograph, quasi-isobare und quasi-isotherme Prozesse) eignet sich zur Charakterisierung der thermodynamischen Stabilität der Verbindungen. Die Temperatur des Beginns der Thermolyse bei linearem Aufheizen zeigt das Erreichen eines definierten Wertes der Geschwindigkeitskonstante an (in Abhängigkeit von der Empfindlichkeit des Fühlers des Gerätes und von den Versuchsbedingungen). Die Temperatursequenz der zunehmenden Thermostabilität stimmt nicht nötigerweise mit der Sequenz der zunehmenden Werte der Aktivierungsenergie überein, da erstere in den meisten Fällen von der Aktivierungsenthropie abhängt.

Резюме — Обсуждена информационная емкость термического анализа при оценке термической стабильности координационных соединений в термолитических процессах, включающих выделение летучих лигандов. Температура термолиза при квази-равновесных условиях (Q-дериватограф, квази-изобарный, квази-изотермический метод) является приемлемой для характеристики термодинамической стабильности соединений. Температура начала термолиза при линейном нагреве означает достижение определенного значения константы скорости и зависит от чувствительности принимающего устройства прибора и экспериментальных условий. Температурный порядок следования увеличения термической стабильности может не совпадать с порядком следования увеличения активационной энергии, поскольку в большинстве случаев он зависит от значения активационной энтропии.