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A STUDY OF THE DEHYDRATATION KINETICS OF BINUCLEAR EDTA CHELATES CaML · nH_2O

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Dehydratation kinetics of aquo-acido complex EDTA chelates CaML · nH_2O ($M =$ $=$ Mn, Co, Ni, Cu, Zn, Cd, Ca, $n = 2 \ldots 5$) were studied under non-isothermal conditions. The existence of two isokinetic temperatures ($\beta_1 = 42°$, $\beta_2 = 216°$) has been detected with a reliability of 95%. The compensation effect found is explained by the change in the number of bonds formed in the sequence of equal-type dehydratation reactions of analogously built-up, but not isostructural compounds.

In an earlier work we studied the dehydratation kinetics if the binuclear EDTA chelates MgML · 6 H_2O and MnML · 6 H_2O (L^{4-} = anion of ethylenediaminotetraacetic acid (EDTA), M = CO, Ni, Cu, Zn). These compounds are asymmetrical binuclear complexes with the structure $[M_I(H_2O)_4O_IO_{II}][M_{II}L] \cdot 2\ H_2O$. The first cation coordinates four molecules of water and two "carbonyl" oxygen atoms of the carboxylic groups of the EDTA ligand, while the second cation coordinates the donor atoms of the organic ligand, i.e. two nitrogen atoms and four oxygen atoms of the four carboxylic groups. The dehydratation process of these compounds is a substitution process of the ligands, by displacement of water and redistribution of the donor atoms of the single EDTA ligand between the two central atoms [1].

We synthetized the analogous series of the chelates CaML · nH_2O (M = Mn, Co, Ni, Cu, Zn, Cd, Ca; $n = 2 \ldots 5$). In this sequence not all compounds are isostructural, but the main principle of their structure is the same: the central calcium atom coordinates mainly water molecules, while the central transition metal atom coordinates the donor atoms of the organic ligand. For instance the structure of the chelate CaCoL · 5 H_2O is $[Ca(H_2O)_3O_IO_{II}O_{III}O_{IV}O_V]$ $[CoL(H_2O)] \cdot H_2O$. The coordination number of calcium is eight, O_IO_{II} is a four-member cycle of the oxygen atoms of one open carboxylic group (unlinked with the central cobalt atom), $O_{III}O_{IV}O_V$ are the "carbonyl" oxygen atoms of the carboxylic groups of adjacent anions of the ligand EDTA. The central cobalt atom coordinates five donor atoms of EDTA and the sixth site is occupied by a water molecule [2].

Experimental details were described earlier. We used a continuous reactor with a helium flow-rate of 120 cm^3/min through the sample, sample mass was 10 mg (100 μm – 400 μm fraction), heating rate was 4 – 6°/min, and evolved gas was recorded using a conductometric detector [3].

For the calculation of the kinetics of the process the integral method, analyzing the linearity of lg g(α) *vs.* $1/T$ was applied [1]. In all cases the beginning of the process could be described by the equation of the shrinking sphere, and we related the calculated kinetic parameters of the process to the chemical reaction at the interphase boundary. The kinetic parameters obtained were reported in [4].

In the present paper we shall deal solely with the questions of mechanism. To analyze the kinetic lability of the chelates it is insufficient to compare the E_a values only (this energy barrier is minimum in the case of the copper chelate). The values of the rate constants at identical temperatures must also be compared. The habitually chosen temperature of 25° to compare rates of reactions in solutions would be unjustified in the present case, since noticeable dehydratation ($k_c = 10^{-4}s^{-1}$) starts with some chelates only at 80 . . . 110°. One could, obviously, compare the temperatures of the start of dehydratation: 119° (Mn), 109° (Cd), 80° (Co), 36° (Ni), 32° (Zn), 21° (Cu), and consider this sequence as the sequence of kinetic stability (at the temperatures at which the identical rate constant of $\sim 10^{-4.6}s^{-1}$ is reached in all dehydratation reactions [5]). This approach is, however, incorrect in the ranges where isokinetic points are present. Let us therefore compare the rate constants. The plot lg k_c *vs.* $1/T$ (Fig. 1) demonstrates the presence of two isokinetic temperatures, $\beta_1 = 48°$, and $\beta_2 = 224°$. Hence the starting temperatures of dehydratation as the measure of their kinetic stability are unsatisfactory.

In the main part of the temperature range of dehydratation (50 . . . 130°) the sequence of stability of the chelates is

$$\mathrm{Mn} > \mathrm{Cd} > \mathrm{Cu} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Zn}.$$

Since an obvious relationship exists between kinetic stability and properties of the central transition metal atom, the following deaquation-anacidation mechanism can be suggested for the chelates in question:

$$[\mathrm{Ca(H_2O)_nO_x}]\ [\mathrm{ML}] \xrightleftharpoons[k_c\,=\,k_i \cdot k]{K_i} [\mathrm{(H_2O)_nCaLM}] \xrightarrow{\mathrm{k}} [\mathrm{CaLM}] + \mathrm{nH_2O}$$

where K_i is the equilibrium constant of the formation process of a more symmetrical binuclear chelate (the process involving in some cases an increased coordination number of Ca), the equilibrium being defined both by the strength of the splitted M–N and M–O bonds and the newly formed Ca–N and Ca–O bonds, and by the entropy component; k is the rate constant of the deaquation process involving the splitting of the Ca–OH_2 bonds; and k_c is the rate constant experimentally observed in the dehydratation process.

The feasibility of an indirect confirmation of this mechanism will be dealt with separately.

The isokinetic temperatures found on the plot lg k_c *vs.* $1/T$ indicate the presence of compensation effects. To check whether true compensation effects appear, it was suggested [6] to analyze three functional relationships: (i) lg k_{T_2} *vs.* lg k_{T_1}; (ii) lg k *vs.* $1/T$; (iii) lg A *vs.* E_a. These recommendations were, however, made for iso-

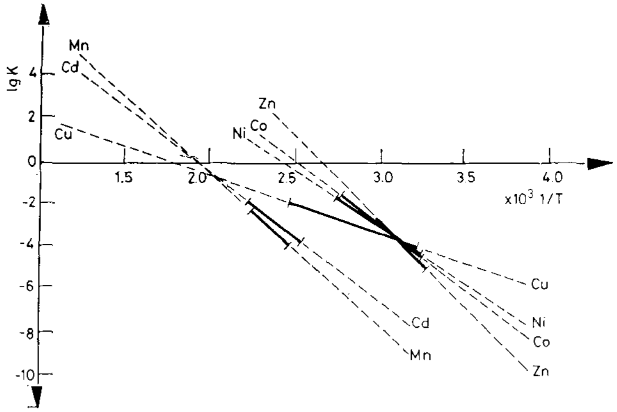

Fig. 1. The relationship lg k_c *vs.* $1/T$ for the dehydratation reactions of the EDTA chelates CaML · nH_2O (M = Mn, Co, Ni, Cu, Zn, Cd). The temperature ranges utilized for the calculation of E_a and A are separated by unbroken lines

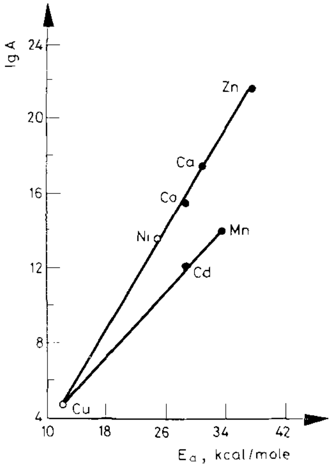

Fig. 2. The relationship lg A *vs.* E for the dehydratation reactions of the EDTA chelates CaML · nH_2O (M = Mn, Co, Ni, Cu, Zn, Cd). For the nickel and copper chelates, the sizes of the errors in the determinations of E_a and A (at a reliability coefficient of 95 %) are marked in the figure

thermal kinetics, where the primary informations are the values k_{T_1} and k_{T_2}. Under non-isothermal conditions, the directly calculated values are E_a and A. The compounds under study demonstrate the presence of compensations effects on the plot lg A *vs.* E_a (Fig. 2).

The question whether the observed phenomena are true isokinetic temperatures always turns up, since there is a possibility, even when the rate constants of all reactions studied are constants, that a slope will appear when represented in the coordinates lg A *vs.* E_a due to experimental errors (error ellipse) [6]. In this case the value β is equal or close to the average experimental temperature.

In Fig. 2, the values E_a and lg A are represented with the error calculated from five experiments with a reliability coefficient equal to 95%. As may be observed, the experimental error is not so large to exclude the trueness of the compensation effect.

The values of the isokinetic temperatures were determined by two methods: from the slope of the straight lines in the coordinates lg A *vs.* E_a ($\beta_1 = 42 \pm 26°$, $\beta_2 = 216 \pm 33°$), and by the pairwise intersection of the straight lines in the coordinates lg k *vs.* $1/T$ ($\beta_1 = 45 \pm 9°$, $\beta_2 = 224 \pm 20°$). In Fig. 1, the temperature ranges utilized for the calculation of E_a and A are separated by unbroken lines. The temperature ranges utilized are those corresponding to the conversion α, in which the kinetics of the process are described by the equation of the shrinking sphere.

The recommended analysis of the relationship lg k_{T_2} *vs.* lg k_{T_1} cannot be strictly carried out for non-isothermal kinetics, since rate constants are only secondary informations, and – as already mentioned – the dehydratation ranges themselves differ, while only that part of the kinetic curve of gas evolution is utilized for the calculations which corresponds to the equation of the shrinking sphere (usually, after conversions of 50 . . . 60% the diffusion of the water vapours evolved to the surface of the spherical particle through the layer of the dehydratated chelate will be the slowest process).

For instance, the dehydratation range for CaCuL · 5 H_2O, $\Delta t°$ is 40 to 130°, that for CaCdL · 2 H_2O, $\Delta t°$ is 131 to 171°. The temperature ranges themselves are broad, and do not even overlap. The total temperature range of the dehydratation of the studied compounds is 21 to 177°. To calculate rate constants we used the temperatures = 293 K and 373 K.

Two straight lines are also obtained in the coordinates lg k_{373} *vs.* lg k_{293}. The slope of the straight line for the copper, zinc, nickel and cobalt compounds is $\kappa_1 = -1.77 \pm 0.65$; $T_1/T_2 = 0.79$. This series is one ot the rather rare cases in which the isokinetic temperature β_1 lies within the $T_1 \ldots T_2$ range [6]. If κ_1 (within the error limits of a reliability coefficient of 95%) differs from the value 1 as well as from the value T_1/T_2, β_1 may be considered not simply the average temperature of the experiment, but the isokinetic point, with a reliability of 95%.

For the copper, cadmium and manganese compounds the slope of the straight line is $\kappa_2 = 0.46 \pm 0.20$; $T_1/T_2 = 0.79$. This is the alternative in which $\beta_2 > T_2$ [6]. In this case the condition of the existence of isokinetic points is that the the difference $(T_1/T_2 - \kappa_2)$ be higher than the error of κ_2 (± 0.20) at a reliability coefficient of 95%. $T_1/T_2 - \kappa_2 = 0.79 - 0.46 = 0.33$. Thus the temperature β_2 can also be considered isokinetic with a reliability of 95%.

It has been reported in the literature that if, in a series of analogous-type reactions, a change in the number of bonds being formed takes place, a strict relationship will be observed in kinetics and thermodynamics between $\Delta H°$ and $\Delta S°$, and the slope in the coordinates ΔH *vs.* ΔS (isokinetic or isoequilibrium temperature) will significantly depend on the strength of the bonds [7]. The chelates $CaMnL \cdot 3\,H_2O$, $CaCoL \cdot 5\,H_2O$, $CaNiL \cdot 4\,H_2O$, $CaCuL \cdot 5\,H_2O$, $CaZnL \cdot 5\,H_2O$, $CaCdL \cdot 2\,H_2O$ are non-isostructural binuclear compounds differing in the number of M – N and M – O bonds, these bonds also differing in strength, and the chemism of the thermal dehydratation process fully corresponds to these concepts.

One may conclude that compensation relationships in thermal kinetics will be observed only in such apparently analogous, but non-isostructural compounds, for which the overall chemical reaction is only apparently the same for the individual members of the series, but in fact involves different numbers of intermediate elementary chemical reactions.

A schematic example for such a series is

$$\begin{aligned}
&[M^{I}L_{VI}] \cdot aH_2O \longrightarrow [M^{I}L_{VI}] + aH_2O\\
&[M^{II}L_{V}(H_2O)] \cdot bH_2O \longrightarrow [M^{II}L_{VI}] + (b+1)H_2O\\
&[M^{III}L_{VI}(H_2O)_2] \cdot cH_2O \longrightarrow [M^{III}L_{VI}] + (c+2)H_2O
\end{aligned}$$

(IV-VI^- being the effective dentateness of the polydentate ligand in the chelate).

If truly identical chemical reactions take place in the thermolysis of isostructural compounds, small differences in the kinetic parameters of the processes will make it difficult to prove that the compensation effect appearing in such cases is not apparent, but a true compensation effect, and one cannot exclude the possibility of isoenthalpy or isoentropy for processes in such series.

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Résumé — On a étudié, dans des conditions non-isothermes, la cinétique de déshydration des chélates complexes aquo-acides de l'EDTA de type $CaML \cdot n\,H_2O$ ($M =$ Mn, Co, Ni, Cu, Zn, Cd, Ca; $n = 2 \ldots 5$). On a établi, avec une probabilité de 95%, l'existence de deux températures isocinétiques ($\beta_1 = 42°$, $\beta_2 = 216°$). L'effet de compensation trouvé s'explique par le changement du nombre des liaisons formées lors des réactions de déshydratation de type similaire des composés de composition analogue mais non isostructuraux.

Zusammenfassung — Die Dehydratisierungskinetik der Aquo—Acido-Komplexe der EDTA-Chelate $CaML \cdot n\,H_2O$ ($M =$ Mn, Co, Ni, Cu, Zn, Cd, Ca, $n = 2 \ldots 5$) wurde unter nicht-isothermen Bedingungen untersucht. Die Existenz zweier isokinetischer Temperaturen ($\beta_1 =$

$= 42°$, $\beta_2 = 216°$) wurde mit einer Wahrscheinlichkeit von 95% festgestellt. Der festgestellte Kompensationseffekt wird durch die Änderung der Zahl der im Laufe der Dehydratisierungsreaktionen ähnlichen Typs analog zusammengesetzter, doch nicht isostruktureller Verbindungen entstandenen Bindungen, erklärt.

Резюме — Кинетика дегидратации халатов ЭДТА (акво-ацидо-комплексов) $CaML \cdot nH_2O$ (M = Mn, Co, Ni, Cu, Zn, Cd, Ca; $n = 2 \ldots 5$). изучена в неизотермических условиях. С 95% надежностью показано существование двух изокинетических температур ($\beta_1 = 42$ °C, $\beta_2 = 216$ °C). Обнаруженный компенсационный эффект объясняется изменением количества образующихся связей в ряду однотипных реакций дегидратации аналогично построенных, но неизоструктурных соединений.