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STEP-BY-STEP PATTERN OF THERMAL DISSOCIATION OF COORDINATION COMPOUNDS

Thermoanalytical study and theoretical considerations

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The problem of the correlation between the initial compound structure (the strengths of the ligand bonds) and the stepwise nature of the thermal decomposition process is discussed from a thermodynamic point of view. The absence of such a direct correlation is shown. This theoretical consideration is verified by experiment.

There is a very popular conviction in the chemical literature that the step-by-step character of thermal dissociation processes is connected with the different strengths of bonding of the molecules lost from the starting compound structure: weakly bonded molecules are removed in the early stages, and more strongly bonded ones later. This model is often used to explain the step-by-step dehydration when hydrates with high water contents (with coordinated and non-coordinated water molecules) are heated. This idea is regularly used in articles describing the thermal stability of compounds, but this approach is not denied in reliable books discussing dehydration problems in detail.

There are articles in which the correlation between the stepwise decomposition, kinetic parameter values and peculiarities of the coordination sphere composition (the lengths of metal-ligand bonds, their lengthening and shortening under heating, anisotropic temperature factors, etc.) are considered [1-3].

It is true that it has been noted [4] that the reconstruction of a mixed aqua polyhedron during dehydration would invalidate conclusions about the difference in the water bonding energies in the starting hydrate on the basis of the thermogravimetric pattern of the stepwise dehydration, but nevertheless it is also stated in this book that the dehydration temperature depends on the strength of the water bonding; in the hydrates of salts, the freedom of

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movement is higher for the uncoordinated water molecules than for the coordinated ones, and this must give rise to a lower temperature of their removal. It is noted that, if there is a transition from a pure aqua complex (polyhedron with high symmetry) to a mixed aqua-acido complex (polyhedron with low symmetry), the bond energy increases only for some of the water molecules, and this can be the cause of the step-by-step dehydration [4].

However, if we deal with the dehydration of multi-water hydrates from the point of view of their thermodynamic stability, it is necessary to have $\Delta H - T \cdot \Delta S = \Delta G < 0$ for the water loss resulting in the next hydrate (with lower water content) formation. The question is: what hydrate can form as a intermediate phase during the dehydration, and is it connected with the features of the location of the water molecules in the starting multi-water hydrate?

For a discussion of stepwise dehydration, let us use the description of the hydrate formation mechanism based on the modified Born-Haber cycle [5-7]. In these works, crystalline hydrate formation from the anhydrous phase is considered to involve two sequential reactions:

1) The structure of the anhydrous crystal is expanded in such a manner that there is room for the gaseous water molecules to enter, and the structure obtained is eqivalent to the hydrate structure.

2) The expanded matrix interacts with water molecules, and covalent and hydrogen bonds are formed.

Energy is absorbed in the first stage (ΔH_1) and is liberated in the second stage (ΔH_2). The vaporization heat (ΔH_v) is included in the value of ΔH_1.

There is a positive entropy contribution because of the crystal expansion, but the total entropy change is always negative, as the entropy decrease is very large when the anhydrous crystal reacts with water (the loss of the translation and rotational degrees of freedom by the water molecules). This means that the reaction of hydrate formation is controlled by the enthalpy: the hydrate can form ($\Delta G < 0$) if $\Delta H_1 + \Delta H_2 = H_w < 0$.

Such a consideration of crystalline hydrate formation from the anhydrous compound shows absolutely clearly that, in the system "anhydrous compound - gaseous water", only those hydrates can be formed for which the total enthalpy change from the structure expansion and from the chemical interaction is negative.

Let us now discuss the process of dehydration of a multiwater hydrate to an intermediate hydrate (with lower water content). The entropy change for such a process is always positive (as discussed above). Therefore the value of $\Delta G'$ is negative if the value of $(\Delta H'_1 + \Delta H'_2)$ is not very large $(\Delta H'_w + T \cdot \Delta S' < 0)$. The role of the entropy contribution is very important: the entropy term controls the reaction of intermediate hydrate formation. There is no correlation between the composition and the structure of the intermediate phase and the existence of weakly and strongly bonded water molecules in the starting hydrate (with higher water content).

It is known that the complexes $[Pt(NH_3)_5Cl]Cl_3 \cdot H_2O$ and $[Pt(NH_3)_6]Cl_4 \cdot H_2O$ do not exist without the added water molecules, which stabilize their structures via the formation of the close packing [8]. If the water molecule is removed, the coordination sphere is destroyed, with ammonia removal. These compounds seem to be examples of the instability of the structure of anhydrous ammonia complexes just because of the entropy contribution.

It is known that the hydrate $MgSO_4 \cdot 4H_2O$ decomposes in an isothermal process in different ways on different shifts from the equilibrium position (Fig. 1 [9]). The tetrahydrate is transformed to the monohydrate at 50° (these phases being the only equilibrium ones in the system). The stepwise dehydration takes place at 85°: the metastable phase $MgSO_4 \cdot 2.2H_2O$ is formed. The tetrahydrate and the intermediate metastable phase have practically the same crystallographic parameters a, b, c and β: the crystal matrix remains expanded after the dehydration (it is worth noting that the parameter b is twice as large in the monohydrate as in the tetrahydrate). This is an example of the independence of the dehydration steps from the starting structure and of the great influence of the equilibrium shift.

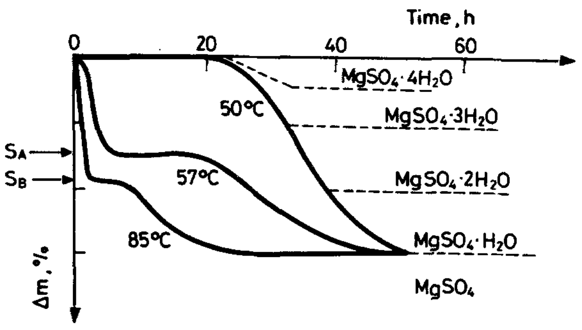

Fig. 1 Isothermal dehydration of $MgSO_4 \cdot 4H_2O$ at different shift from the equilibrium position [9]. The pressure in the system is about 0.013 atm

The general conclusion is that the compositions of the intermediate phases during the thermal dissociation of coordination compounds (dehydration as a particular case) can not be connected with the peculiarities of the structure of the starting multi-ligand compound (the hydrate with higher water content). From a thermodynamic point of view, the structure (and its thermodynamic characteristics) of the final non-complexed salt (anhydrous compound) has an effect on the compositions of the intermediate phases.

A more common example, verifying this point of view, is the existence of many intermediate stable phases during the thermal dissociation of complex compounds under a high pressure of the evolved gas, the reduction of their quantity under a lower gas pressure and the disappearance (rather frequent) of these intermediate phases during decomposition under vacuum.

Quasi-equilibrium thermogravimetry is an ideal thermoanalytical method to prove the peculiarities of thermal dissociation discussed above.

Two isostructural EDTA chelates, $Mg_2L\cdot 9H_2O$ and $MgMnL\cdot 9H_2O$ $/[M_I(H_2O)_6][M_{II}L(H_2O)]\cdot 2H_2O/$, contain three different groups of water molecules. The dehydration steps are not connected at all with this different bonding of the water molecules: there is no step of loss of two weakly bonded uncoordinated water molecules. The Mg-Mg complex forms the tetrahydrate, which decomposes with the formation of phases with various compositions. The Mg-Mn chelate forms stable individual phases of the trihydrate and dihydrate (Figs 2 and 3).

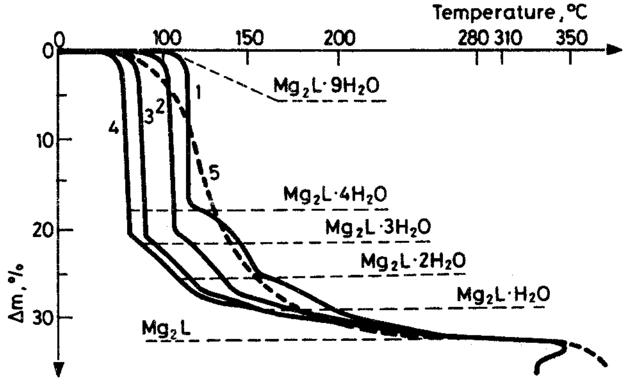

Fig. 2 Dehydration of EDTA chelate $Mg_2L.9H_2O$ under quasi-equilibrum conditions. Sample holders: 1-labyrinth holder, 2-crucible with lid, 3-open crucible, 4-polyplate holder (quasi-isothermal heating, $q = 0.5$ mg/min), 5-open crucible, linear heating (5 deg/min)

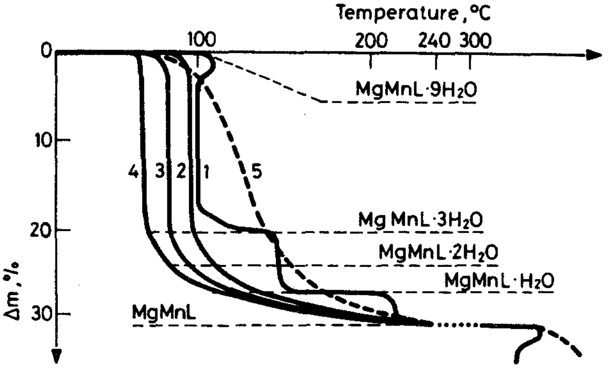

Fig. 3 Dehydration of EDTA chelate $MgMnL.9H_2O$ under quasi-equilibrum conditions. The designations are on Fig. 1

If one tries to explain the step-by-step pattern of the thermal dissociation process in terms of the different bond strengths of the liberated molecules, it will be difficult to understand the increase in the number of steps (number of intermediate phases) when the process is shifted to the high-temperature region, and the one-step run of the process at low temperature under vacuum (or in an inert gas flow). However, the thermodynamic explanation is absolutely understandable: the intermediate phase does not exist under low pressure of the gas product ($\Delta G' > 0$); the value of $\Delta G'$ becomes smaller (because of the increase in the term $T \cdot \Delta S'$) with increase of the pressure and temperature, and the intermediate phase appears as a result of decomposition, when the value of $\Delta G'$ becomes negative ($\Delta H'_w < T \cdot \Delta S'$).

One more example is the thermal decomposition of an inclusion compound formed from a coordination compound. On heating, β-[Ni(4-MePy)$_4$(NCS)$_2$]·(4-MePy) decomposes as a phase of variable composition (Fig. 4); the intermediate metastable β-phase collapses into two solid phases: β-[Ni(4-MePy)$_4$(NCS)$_2$]·(4-MePy) and α-[Ni(4-MePy)$_4$(NCS)$_2$]. The newly formed inclusion compound decomposes to the α-matrix of the host. Such stability features are connected with a complex combination of the thermodynamic stability and kinetic stability of several phases in the temperature region 50-200^0 under the pressure of the gas product (the guest) in the interval 0.05-1.0 atm.

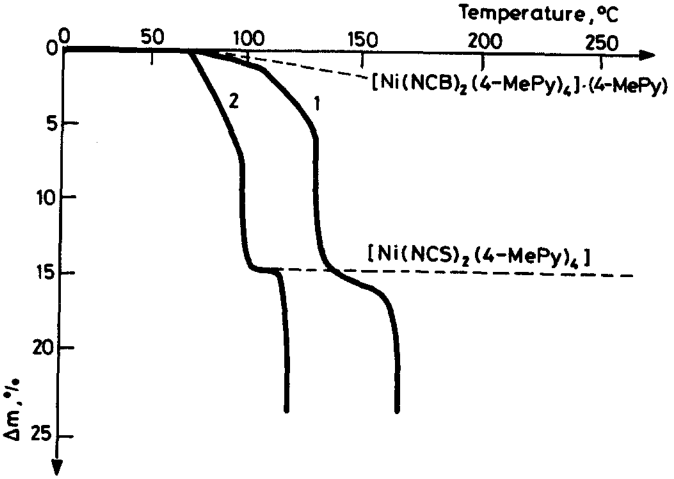

Fig. 4 Thermal decomposition of the inclusion compound β-[Ni(4-MePy)$_4$(NCS)$_2$]·(4-MePy) under quasi-equilibrium conditions (quasi-isothermal heating, $q = 0.1$ mg/min). Sample holders: 1-labyrinth holder, 2-crucible with a lid

Conclusions

After these considerations, it is clear that there is no physico-chemical meaning in the connection between the starting structure of the compound and the predicted stepwise character of thermal dissociation (and intermediate phase compositions). Any such coincidence observed is only an accidental coincidence, which can manifest itself only under fixed experimental conditions, and can therefore be regarded only as a spurious coincidence.

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Zusammenfassung — Vom thermodynamischen Gesichtspunkt her wurde die Frage der Korrelation zwischen der Struktur der Ausgangsverbindung (Stärke der Ligandenbindung) und der Mehrstufigkeit des thermischen Zersetzungsprozesses erläutert. Es wird gezeigt, daß solch eine Korrelation nicht besteht. Diese theoretische Feststellung wird experimentell bestätigt.