Stability and reactivity of coordination and inclusion compounds in the reversible processes of thermal dissociation

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Abstract

The thermoanalytical approach to the study of the kinetic lability of coordination and inclusion compounds in the reversible processes of thermal dissociation is discussed. The secondary crystal structure that existed initially and its transformation into the reaction zone on the surface of the grain are considered. It is pointed out that in any experiment the measured decomposition rate is averaged over all crystal faces. Kinetic data can be interpreted in terms of the transformation mechanism only for a series of isostructural compounds. The author's own experimental data on thermal dissociation processes for coordination and inclusion compounds are presented and considered. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Coordination compounds (with neutral ligands) and inclusion compounds (clathrates) are very interesting and favored materials for thermoanalytical investigations. One reason for this is the clear-cut stoichiometry of the thermal decomposition reactions. There is no total destruction of the component molecules and ions (and only for these substances the *thermal decomposition* is called *thermal dissociation*). Both coordinated molecules of the inner coordinated sphere, and included guest molecules from channels and cages of the host matrix of water, ammonia or organic amines, acids, alcohols, etc. evolve in reversible and step-by-step processes. It is easy to isolate and to characterize intermediate phases and in the so-called "quasi-equilibrium" experiment the most likely phases are thermodynamically stable [1]. It is possible to carry out kinetic thermoanalytical experiments (with either linear heating or by CRTA) and to calcu-
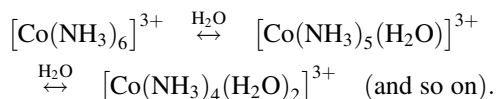
late kinetic parameters for each step. It is also possible to synthesize a representative series of coordination compounds, differing from one another only in their central atoms or ligands in the first coordination sphere, or by outer sphere ions, and a series of inclusion compounds with one host matrix differing from one another by guest molecules. This provides the way to find the general trend of kinetic lability throughout the series.

In a general sense, reactions involving the thermal dissociation of coordination compounds are the heterogeneous processes of ligand substitution. In some cases one can find the reaction that is formally identical to a substitution reaction in solution, e.g.

$$[Co(NH_3)_6]Cl_2 \overset{\Delta H}{\rightarrow} [Co(NH_3)_2Cl_2] + 4NH_3 \uparrow$$
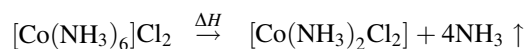
The solvation in solution always changes over any transformation of the coordination sphere into the ligand substitution process with possible conservation

of the coordination number, and the coordination of solvent molecules makes it possible to obtain in the solution a large number of partially substituted forms ("stepping equilibrium"):

$$\left[\text{Co(NH}_3)_6\right]^{3+} \overset{\text{H}_2\text{O}}{\leftrightarrow} \left[\text{Co(NH}_3)_5(\text{H}_2\text{O})\right]^{3+}$$
$$\overset{\text{H}_2\text{O}}{\leftrightarrow} \left[\text{Co(NH}_3)_4(\text{H}_2\text{O})_2\right]^{3+} \quad (\text{and so on}).$$

The topochemical control over the solid state reactions, and also thermodynamic and kinetic restrictions lead to a very small number of intermediate phases in the intricate reaction of the thermal dissociation of the initial (high-ligand) complex compound to the final product, a simple salt or a complex still containing non-volatile ligands. With regard to inclusion compounds, for example, most of the *first stage* layered compounds of graphite fluoride $C_2F\cdot nA$ (fully filled by guest molecules such as alcohols, amines, etc.) are stable only in the presence of the supernatant liquid of the guest. So one cannot always form the most convenient series of compounds for study with absolutely identical decomposition reactions for comparison.

The necessity for quantitative characterization of such thermal dissociation process, both for coordination and inclusion compounds, stems from the fact that it is the only way for the creation and progress of solid state chemistry in the study of these compounds. In the well-established context of modern coordination chemistry, it will permit discussion of the kinetics of heterogeneous ligand substitution processes, associative and dissociate mechanisms of such substitutions, trans-influence and mutual influences of ligands in the coordination sphere, and energy of extra-stabilization in the complexes of d-block elements. For inclusion compounds, it will help to understand the nature of their structural stability and to discriminate between the thermodynamic and kinetic contributions in such stabilization.

It is as well to recognize that there is a sharp prejudice against thermoanalytical macrokinetics. This prejudice is based both on the mistakes of scientists, in experimental procedure, data treatment and interpretation of results, and on real problems and contradictions of heterogeneous (solid state) kinetics.

Of real interest are unavoidable problems and contradictions:

1. The validity of the Arrhenius equation for the description of solid state kinetics is not evident. This problem has been studied in theoretical work, devoted to the consideration of the elementary act of atomic rearrangement in the solid state [2]. The calculations were performed in the framework of Sleiter's model for one-dimensional and three-dimensional reaction models. The mathematical expression for the rate constant has been worked out in two cases. At *high temperature*, the rate constant of the bond rupture decreases in proportion to the reciprocal temperature $(1/T)$, but this high temperature is suited to the requirements of the atom displacement from the equilibrium position beyond the lattice parameter (d), and has nothing to do with the solid state description.

At *low temperature*, the rate constant of the bond rupture has the Arrhenius temperature dependence, and in this case the pre-exponential factor is of the order of the maximum photon frequency in the crystal (W_d). The elementary act of the rearrangement is not connected with the formation of a long-lived intermediate state and proceeds fully in a time that is comparable with the minimum period of atomic oscillation in the crystal [2].

It is reasonable to suggest that if such a long-lived intermediate state does not really occur in the simple phase transition processes, it can exist in thermal dissociation reactions, including complex rearrangement of dozens of atoms during the change in coordination sphere or the included gas release.

2. The real structure of the particle of decomposing substance is very important. A large body of recent data points to the deficiency of the traditional solid state model, based only on the atomic structure of crystals. Various experiments including the observed intensities of diffraction lines, "dimensional effects" in crystals, the anisotropy of diffusion coefficients in isotropic crystals, the limiting values of solid solution, etc. point closely to the existence of a *secondary crystal structure*. According to this concept, any single crystal always consists of microregions, i.e. microblocks of size 10^{-4}–10^{-6} cm. Many works have dealt with this problem in different terms since 1914 [3], and it is now widely known and

generally accepted as being correct. This problem is the subject of a comprehensive discussion in [4].

3. It is well known that the surface structure of crystal faces is not like the bulk of these crystals. In the crystals of such metals as Pb, Al, Au, Cu and W, the surface interplanar spacings are squeezed, with distances shortening from 3% to 58%. On the other hand, the deformation of the surface for ionic crystals results in an increase of the interplanar spacings (for the first five surface layers the increase is as much as 2–11%) [5]; for the crystals of the noble gases, xenon and argon, this increase reaches 3.5% [5,6]. On surface of organic molecular crystals, several layers are so disordered that their features are close to those of the melt [7]. The surface of ice has imperfections (steps of molecular size) and gains mobility already at -140°C and is liquid-like from -30°C; the thickness of this water film is 10 monomolecular layers [5].

There are so-called "chemical sublimation" processes, involving interaction of the active gas with the solid substance and sublimation of the compound formed; e.g., $Si_{(s)} + 2Cl_{2(g)} \rightarrow SiCl_{4(g)}\uparrow$. Since the experimental rates of such a chemical sublimation do not depend on the reacting crystal face, it is suggested that the reactive surface layer (being produced by the initial chemical sorption) is uniform for all crystal faces [8]. For single crystals of Mo, Ni and Ag the rates of the atomic vaporization are equal for different crystal faces [9], and the specific catalytic activity of metallic and oxide catalysts does not depend on the crystal face chosen [10].

The most significant example is the very anisotropic layered compound graphite. For the ideal single crystal the ratio of the reaction rates on the different crystal faces must reach a factor of 10^{15} times, but for real graphite single crystal this ratio is reduced to only 100-fold [11].

4. Some new results of the study of decomposition kinetics are of fundamental importance. The study of the dehydration process of single crystals of $Li_2SO_4 \cdot H_2O$ showed that the difference between the transformation rates for the sections of different crystallographic orientation is very small ($V_{010}/V_{101} = 1.17$), although the crystal structure is significantly anisotropic [12]. All water molecules in the elemental cell are equivalent; they are bonded with SO_4^{2-} — anions (by hydrogen bonds) and with Li^+ — cation (by the coordination bond) and are arranged in a zigzag fashion. This pronounced chain motif is responsible for the anisotropy of the crystal structure: the crystal face (0 1 0) is perpendicular to the chains of water molecules, and the (1 0 1) plane is parallel to these chains.

Furthermore, tablets compacted from polycrystal powder (with dominant size 0.4–0.5 µm), have absolutely the same kinetic parameters as single crystals, when the tablet density reaches 92–98% of the theoretical density for the single crystal. The explanation of such behavior is the identity of the make up of the reaction zone in all these three cases; the "product–reagent" interface is parallel to the decomposing crystal face or to the tablet surface, the reaction zone consists of a set of blocks with interface boundaries clearly seen by scanning election microscopy, and the average block size is 5×10^{-7}–7×10^{-7} cm. The water is eliminated unhindered from all block faces.

It was noted that small fragments, 5×10^{-5} cm in size and extended like rice grains, are formed during the dehydration of large blocks. Their pattern may be different; the (1 0 1) planes may be packed in an orderly fashion, being mutually perpendicular to one another, or they may be disordered. Such a fragment appears to be the elemental reacting block [12]. These small fragments do not break up during repeats of the rehydration–dehydration experiments.

Worthy of mention are the known considerations of the actual activated volume for the reaction in the condensed state. For supercooled liquid flow it was shown that the "elementary act" of relaxation (with the bonds breaking and relative orientation) demands simultaneous involvement of the whole group of atoms. The number of such structural elements or atoms, involved in this change, does not depend on the nature of the substance and runs into hundreds [13,14]. In the rigid solid body the instantaneous local distortion of the crystal lattice must capture the greater volume.

In solid state chemistry the term elemental reacting block implies the minimum volume, in which the chemical transformation proceeds simultaneously

and instantly by a ''trigger'' mechanism [15]. For the phase transformation *monoclinic sulfur → rhombic sulfur* (or the recrystallization of Al) the amount of instantly reacting molecules is estimated as 10^7, and the reacting crystal volume is estimated as 10^{-15} cm^3 [15,16]. All this can explain the large range of calculated pre-exponential factors in the series of compounds.

Two principal conclusions are important for the validity of kinetic studies in the solid state chemistry of coordination and inclusion compounds. The originally existing microblock system (known as the *secondary crystal structure*) on the disordered crystal surface breaks down into a set of rather independent decomposing blocks. We can study the kinetics of the thermal dissociation only in this surface reaction zone, where the bonds are lengthened and the transformed structure does not have the known detailed structure of the bulk solid. This surface reaction zone involving decomposing blocks will be reproduced and move to the grain center. There is no way to investigate the chemical decomposition reaction on the chosen crystal face, so we will inevitably study the rate of the simultaneous decomposition mentioned above, involving microblock surfaces within the reaction zone that is formed. Only the average rate of decomposition can be registered and calculated. So the spherical grain model is not the mental picture, simplifying the real anisotropic microcrystal. The spherical grain model is representative enough for the decomposing microcrystal in sublimation, thermal dissociation and chemical (solid + gas) reaction. So as the decomposition reaction is reversible, there will be no accidental advancing decomposition front of the reaction zone, because the pressure of the gas released will suppress the reaction.

It is reasonable to expect the identical path of the aforementioned initial surface disordering for a specially organized series of compounds, such as a series of isostructural coordination compounds distinguished by central atoms or by ligands in the first coordination sphere, or by outer sphere ions and a series of inclusion compounds with common host matrix distinguished from one another by guest molecules or, quite the reverse, with a different host matrix. So the analysis of the general trend in the variation of kinetic parameters in the series of isostructural compounds is the only possible use of kinetic studies.

The existence of the so-called *iso-enthalpy* series ($E_i \approx$ const.), iso-entropy series ($A_i \approx$ const.) and the series with *compensation dependence* ($\log A_i = aE_i + b$) is very significant and can be interpreted in terms of the transformation mechanism. It is worth noting that here we do not consider the so-called compensation effect from the point of view of actual compensation between the enthalpy and entropy terms in known kinetic or thermodynamic equations. We only point out that the distribution of compounds throughout these three just mentioned dependencies is important during the investigation of large enough series of coordination or inclusion compounds, chemically related to one other.

2. Experimental

The complexes with aniline and their derivatives (described in the literature long ago) were synthesized by well known methods, while inclusion compounds on the basis of a matrix of coordination compounds (as well as the matrix itself) were synthesized in the systems ''solid salt — liquid organic amine'' [17].
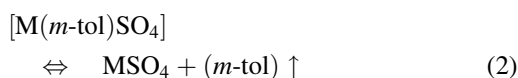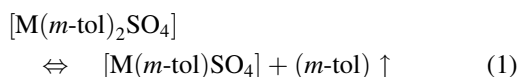
Quasi-equilibrium thermogravimetry [18] was used to investigate the step-by-step character of the thermal dissociation processes and to check the thermodynamic stability of intermediate phases. The full set of sample holders was used (from plate-like to labyrinth design), the sample mass was 150 or 200 mg, constant mass loss rate was the minimum possible (0.16 or 0.3 mg min^{-1}), and the atmosphere was static air.

A home-made gas-flow reactor with conductometric detector was used as the EGA-device for the kinetic experiments [19]. Helium flow rate was 60–160 cm^3 min^{-1}, the sample mass was 5 or 10 mg, and the linear heating rate was in the interval from 2 to 10°/min The size fraction of the grains was within narrow limits: 100–400 µm ($d_{max}/d_{min} < 5$). Kinetic analysis of the gas evolution curves was carried out using the integral method; selection between the different topochemical equations was carried out by linearity of the function lg $g(\alpha)$ vs $1/T$, using the computer program of Sestak and Skvara [20,21]. A search involving 13 equations (based on nucleation, nuclei growth, reaction on the interface, and diffusion) was made; and only if the rate-controlling process was the chemical

reaction at the interface (the equation of the contracting sphere, $d\alpha/d\tau = k(1-\alpha)^{2/3}$, in the range of fraction reacted $0.05 \leq \alpha \leq 0.60$), was the calculated kinetic data used for further discussion. The iso-conversion method [22] was sometimes used for the estimation of the activation energy. Activation energies and pre-exponential factors were calculated as the average from five separate experiments. The calculated errors for them were usually within the range from 5% to 10%.

3. Results and discussion

There are examples of the thermoanalytical approach to the quantitative of the chemical reactions associated with the thermal dissociation of a series of compounds, in which certain suggestions on the mechanism can be made. The thermal dissociation of a series of complexes with *m*-toluidine [M(*m*-tol)$_2$SO$_4$] (M = Mn, Co, Ni, Cu, Zn, Cd). Co-, Zn- and Cd-complexes have been shown to decompose step-wise under quasi-equilibrium conditions, when the partial pressure of *m*-toluidine is not more than 1 atm:

$$[\text{M}(m\text{-tol})_2\text{SO}_4]$$
$$\Leftrightarrow \quad [\text{M}(m\text{-tol})\text{SO}_4] + (m\text{-tol}) \uparrow \qquad (1)$$

$$[\text{M}(m\text{-tol})\text{SO}_4]$$
$$\Leftrightarrow \quad \text{MSO}_4 + (m\text{-tol}) \uparrow \qquad (2)$$

Under the same conditions the Ni-complex decomposes at once to the simple salt:

$$[\text{Ni}(m\text{-tol})_2\text{SO}_4] \quad \Leftrightarrow \quad \text{NiSO}_4 + 2(m\text{-tol}) \uparrow \qquad (3)$$
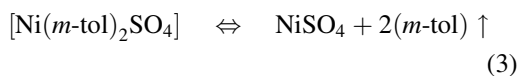
It is evident that phase [Ni(*m*-tol)SO$_4$] is not stable and cannot be obtained through this decomposition.

The kinetics of these reactions have been studied. The compensation effect was observed for all four complexes as shown in Fig. 1, although the stoichiometry of the reactions is different (Eq. (1) or Eq. (3)).

We have synthesized the [Ni(*m*-tol)SO$_4$] complex in solution by a special procedure and studied the decomposition kinetics for both Ni-complexes:
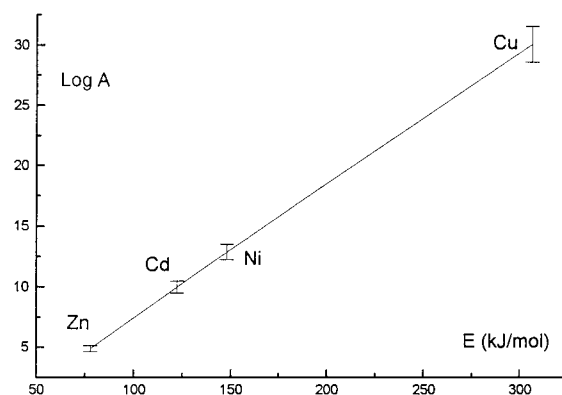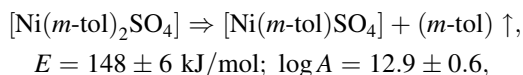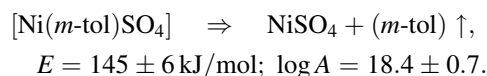
$$[\text{Ni}(m\text{-tol})_2\text{SO}_4] \Rightarrow [\text{Ni}(m\text{-tol})\text{SO}_4] + (m\text{-tol}) \uparrow,$$
$$E = 148 \pm 6 \text{ kJ/mol}; \ \log A = 12.9 \pm 0.6,$$

Fig. 1. Kinetic data for the thermal dissociation process [M(*m*-tol)$_2$SO$_4$] → [M(*m*-tol)SO$_4$] + (*m*-tol)↑.

$$[\text{Ni}(m\text{-tol})\text{SO}_4] \quad \Rightarrow \quad \text{NiSO}_4 + (m\text{-tol}) \uparrow,$$
$$E = 145 \pm 6 \text{ kJ/mol}; \ \log A = 18.4 \pm 0.7.$$

The only difference in the kinetic lability of these two complexes is associated with the entropy factor. The initial temperatures of the decomposition (when $k_0 \approx 10^{-5} \text{ s}^{-1}$) observed are 171°C for the [Ni(*m*-tol)$_2$SO$_4$]-complex, but only 56°C for the [Ni(*m*-tol)SO$_4$]-complex. So the Ni(*m*-tol)SO$_4$]-complex is unstable under the specified conditions and can only be synthesized in the presence of liquid *m*-toluidine.

The transition state structure is believed to be identical for all [M(*m*-tol)$_2$SO$_4$]-complexes, and the initial decomposition reaction is the loss of one *m*-tol-molecule, but for the Ni-complex the intermediate phase is kinetically unstable and immediately decomposes to the stable salt.

The reversible processes of thermal dissociation of the coordination compounds, [M(4-MePy)$_4$(NCS)$_2$], where M = Mn, Cu, Cd, and clathrates with these matrices, [M(4-MePy)$_4$(NCS)$_2$]·0.67(4-MePy), have been studied. They have a trigonal structure. The 4-MePy molecules are tightly bound in the coordination sphere by M–N bonds and are confined to the matrix cavities by van der Waals forces. A peculiarity of these compounds is that for the Cu-clathrate the initial matrix, host complex [Cu(4-Mepy)$_4$(NCS)$_2$], is thermodynamically unstable and does not exist in the system "Cu(NCS)$_{2(\text{solid})}$–4-MePy$_{(\text{liquid})}$", the so-called contact stabilization of host molecules during clathrate formation [23].

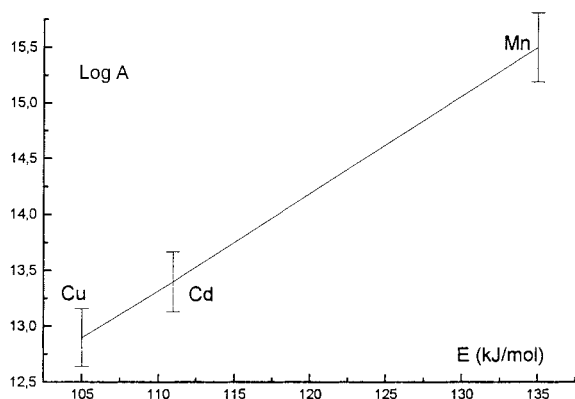Fig. 2. Kinetic data for the thermal dissociation process [M(4-MePy)$_4$(NCS)$_2$]·0.67(4-MePy) → [M(4-MePy)$_2$(NCS)$_2$] + 2.67(4-MePy).

Both the clathrates, [M(4-MePy)$_4$(NCS)$_2$]·0.67 (4-MePy), and the existing host complexes, [M(4-MePy)$_4$(NCS)$_2$] where M = Mn, Cd, decompose instantaneously to [M(4-MePy)$_2$(NCS)$_2$]. The similarity in reaction mechanism for these clathrates is supported by the compensation effect (Fig. 2); the kinetic parameters in the series correlate with the known length of the metal-MePy-ligand bonds inside the coordination spheres of the clathrates (L_{Mn-N} = 2.34 Å, L_{Cd-N} = 2.49 Å, L_{Cu-N} = 2.51 Å). We can conclude that the kinetic stability of clathrates depends mainly upon the stability of the host complex matrix, partly changed by the framework of the clathrate. The change in the length of the metal-ligand bonds explains why [Mn(4-MePy)$_4$(NCS)$_2$] exists as a stable phase but [Cu(4-MePy)$_4$(NCS)$_2$] does not.

4. Conclusions

The reversible processes of thermal dissociation of solid coordination compounds and solid inclusion compounds are typical chemical reactions, but take place within topochemically organized space. The reversibility of these processes suppresses the non-controlled nuclei growth beyond the reaction zone and simplifies the kinetic analysis. The reaction zone is formed on the grain surface from the existing *secondary crystal structure* and includes rather independent

microblocks, decomposing over their whole surface. These processes are suitable for quantitative study by thermoanalytical methods, but the measured decomposition rate is always the average of rates from different crystal faces. The interpretation of the kinetic data suggests a possible explanation of the transformation mechanism, but such a suggestion can only be made investigation of a series of isostructural compounds [24].

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