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SOLID STATE COORDINATION CHEMISTRY
The quantitative thermoanalytical study of thermal dissociation reactions

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Abstract

Physicalo-chemical importance of the quantitative study of kinetic liability of coordination compounds in thermal dissociation processes is considered. Much attention is given to the proof of the physicalo-chemical meaning and validity of kinetic parameters calculated from thermoanalytical data. Experimental data (thermal dissociation of coordination compounds and clathrates with such a matrix) are discussed.

Keywords: coordination compounds, kinetics, thermal dissociation

Introduction and discussion

Coordination compounds (with neutral ligands) are very interesting and favorable materials for thermoanalytical investigations. One of the reason is the clear-cut stoichiometry of thermal decomposition reactions: there are no thorough destruction of component molecules and ions (and only for these substances the thermal decomposition is called thermal dissociation). Molecules coordinated in the inner coordinated sphere (water, ammonia and organic amines, acids, alcohols, etc.) evolve in the reversible (as a rule) step-wise processes. It is easy to isolate and to characterize intermediate phases (and in so-called 'quasi-equilibrium' experiment the most likely these phases are thermodynamically stable). It is possible to run properly the kinetic experiment (in non-isothermal conditions) and to calculate kinetic parameters for each step. It is possible to synthesize representative series of coordination compounds (by the modification of central atoms or ligands in coordination spheres); this provides the way to find the general trend of kinetic liability through the series and its correlation with the modification of this kind.

In general sense the reactions of thermal dissociation of coordination compounds are the heterogeneous processes of ligand substitution. The solvation in the solution always change over any transformation of the coordination sphere into the ligands substitution process with the possible conservation of the coordination number, and the coordination of solvent molecules makes possible to realize in the solution a big number of partially substituted forms ('stepping equilibrium'):

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The thermodynamic and kinetic restrictions lead to very small number of the intermediate phases in the topochemical reaction of the thermal dissociation of the initial (high-ligands) complex compound to the final product. So one can not always forms the most convenient series of studied compounds with absolutely identical decomposition reactions for the correct comparison.

Nevertheless, such approach allows to interpret the reactivity of coordination compounds (in thermal dissociation processes) in correct physicalo-chemical terms and to discuss the kinetics of ligands substitution processes.

During last 25 years hundreds publications in this area create solid state coordination chemistry, and the majority of studies are performed by chemists, deeply involved in thermoanalytical investigations in the frames of the non-isothermal kinetics. Let us note some problems and contradictions of the heterogeneous (solid state) kinetics, usually not discussed.

The validity of the Arrhenius equation for the description of the thermal dissociation kinetics (for solid state processes) is not so evident. This problem was studied recently in the theoretical work, devoted to the consideration of the elementary act of the atoms rearrange in the solid state [1]. 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 was obtained for two cases. Under 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.

Nonetheless under 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, comparable with the minimum period of atoms oscillation in the crystal.

There is no assurance for the uniqueness of a solution of the reverse problem while searching the kinetic topochemical equation. The selection of the kinetic equation is rather formal, and so it is a danger, that the found analytical description is not in agreement with the real movement of the interface. Homotectic topochemical model of the chemical reaction on the microcrystal surface $\{d\alpha/dt=k(1-\alpha)^{0.67}\}$ conforms to the spherical geometry and isotropic properties of the decomposing grain. This approach simplifies the complexity of the decomposition process, so as the anisotropic extended zone (with the depth of dozens interplanar spacings) is thought to exist in the reality instead of idealized two-dimensional interface on the three-dimensional ball surface.

Chemists, working with non-isothermal kinetics, usually think that these listed problems are connected with understandable approximations. It is worth to note that as has already been intimated [2], the popular, useful (and in service today) classical conception of the molecular structure is not consistent with the requirements of quantum mechanics (so as coordinates, momentum and energy are fixed at a time).

Let us discuss the considerable evidence in favour of the physicalo-chemical meaning and validity of kinetic parameters calculated from thermoanalytical data. Some results of the study of decomposition kinetics, arisen in the literature, is of fundamental importance.

Under the study of the dehydration process of single crystals $Li_2SO_4{\cdot}H_2O$ it was found, that the difference between the reaction rates for the sections of different crystallographic orientation is very small (V_{010}/V_{101}=1.17), although the crystal structure is significantly anisotropic [3]. 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 zigzag fashion. This pronounced chain motive is responsible for the anisotropy of the crystal structure: the crystal face (010) is perpendicular to the water molecules chains, and (101) is parallel to these chains.

It was discovered that the 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 one for the crystal). The explanation of such behavior is the identity of the reaction zone constitution in all these three cases: the interface ‘product–reagent’ is parallel to the decomposing crystal face (or to the tablet surface), the reaction zone has the ‘block’ structure (with clear boundaries) and the medium block size is 50–70 μm ($5{-}7{\cdot}10^{-7}$ cm). The water is eliminated unhindered from all block faces.

The significant verification of the averaging of the reactivity for different faces of the anisotropic crystal is the graphite. The relationship between reaction rates on the different crystal faces must be 10^{15} for the ideal crystal, but in experiments with the real crystal it is only 10^2 [4].

There are processes of so-called ‘chemical sublimation’ (the interaction of the active gas with the solid and the sublimation of the formed substance: $Si+2Cl_2 \rightarrow SiCl_4\uparrow$). It is known that the experimental rates of such ‘sublimation’ do not depend on the reacting crystal face. It is suggested that the initial chemical sorption produces the reactive surface zone, which is uniform for all crystal faces [5].

For single crystals of Mo, Ni and Ag the rates of the atoms vaporization are equal for different crystal faces [6], and the specific catalytic activity of metallic and oxidic catalysts does not depend on the crystal face choosing [7].

It is worth to note the existence of the problem of the secondary crystal structure. According to this concept all single crystals always consist from discrete microregions-microblocks the size of 10^{-5}–10^{-6} cm. The long-range order in crystals exists only within such microblock. A lot of works are dealt with the problem in different terms since 1914 [8], and now it is well known and generally accepted as correct. Varied experiments (the observed intensities of diffraction lines, ‘dimension effects’ in crystals, the anisotropy of diffusion coefficients in isotropic crystals, the limiting values of impurities solubility etc.) correspond closely to the existence of such secondary crystal structure. This problem is the subject of considerable discussion in [9].

On the other hand it is well known, that the surface structure of the crystals differs in significant way from the bulk regular one: the interplanar spacings are enlarged (in the first 5 surface layers of ionic crystals the increase is 2–11% [10]), for the crystals of the noble gases this increase lies in the range 0.04 to 3.5% [10–11]. For the organic molecular crystals several surface layers are so disordered, that their features are close to the melt [12]. The ice surface gains the mobility and has imperfections (steps of the molecular size) already at –140°C and is liquid alike from –30°C; the thickness of this water film is 10 monomolecular layers [10].

Two principal conclusions from these considerations are important for the study of the decomposition macrokinetics by the thermoanalytical methods.

1. The surface structure differs significantly from the regular crystal structure, the reaction ability of surface centers is averaged. It is important, that the surface layers are so distorted, that the initially existing anisotropic microblocks system (so-called secondary crystal structure) breaks down into the set of independent microblocks. The thermal dissociation process takes place simultaneously on all surfaces of these blocks (within the created reaction zone) and this leads to the rates averaging over different crystal faces. These circumstances leads to the loss in the anisotropy of chemical properties along the different crystallographic directions, the reactivity of the different faces is drastically leveled. After the formation of such a reaction zone initially disordered surface layers (involving microblocks) are reproduced during the decomposition reaction and move to the grain center directly ahead the reaction zone.

So for the reaction of thermal dissociation the spherical grain model (with the pseudo-homogenous reaction zone, homotetically moving from the surface to the center), is not the mental picture, simplifying the more complex real anisotropic crystal. Therefore if the solution of the reverse problem (from the data of the correctly run experiment) with the searching of the best kinetic description gives the equation $d\alpha/d\tau=k(1-\alpha)^{2/3}$, it describes the real rate of the chemical reaction (transformation of coordination sphere) topochemically realized on the interface.

2. We can study the kinetics of the decomposition reaction only in this specific reaction zone, where the molecules are distorted, the bonds are lengthened, and the transforming structure is not the known one of the bulk solid. Even though we try to investigate the chemical reaction on the choosing crystal face, we will inevitably study the simultaneous decomposition of surfaces of originated microblocks. So the obtained kinetic data is not associated very strictly with the known detailed structure and can not be discussed for a single compound in direct correlation with bonds lengths, angles, octahedron or tetrahedron disorders, etc. Naturally there is a hope (and a reason) to expect the identical trend of this sort of disordering on initial surface for specially organized series of compounds: say, series of isostructural (or analogously constructed) coordination compounds (with modification of central atoms or inner sphere ligands, or outer sphere ions). The analysis of the general trend of the varying of kinetic parameters in such a row of compounds – here is the only possibility in the use of kinetic studies. The existence of so-called iso-enthalpy ($E_i\approx$const.) or iso-entropy ($A_i\approx$const.) series, or the series with compensation dependence ($\lg A_i=aE_i+b$) is very significant and can be interpreted in terms of transformation mechanism.

Experimental

We have used Quasi-equilibrium thermogravimetry (Derivatograph-C and Q-1500-D with the total net of sample holders) for checking the thermodynamically stable intermediate phases. The home made gas-flow reactor with conductometric detector was used as EGA-device for works in the non-isothermal kinetics, the sample (5 or 10 mg, the grain size within narrow limits 100-400 μm) was heated linearly at a rate 4 or 5°C min^{-1}, the helium flow through the sample was 60–200 $\text{cm}^3\ \text{min}^{-1}$.

The kinetic analysis of the gas evolution curves was carried out by the integral method of Šesták and Satava with the computer program TA 1B [13–14]. The equation best describing of all the processes ($0.05<\alpha>0.60$) was the equation of a contracting sphere:

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

We studied reversible processes of thermal dissociation of coordination compounds $[MX_2A_4]$ and clathrates with these matrix $[MA_4X_2]{\cdot}nA$ (M=Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd; A=Py, 4-MePy, H_2O); X=NCS, NO_3, NCO; n=0.67 or 1, or 2), having tetragonal, trigonal or rhombic structures. Four Py and MePy molecules are tightly bounded in the coordination sphere by M–N bonds and others are confined in the matrix cavities by van der Waals forces. A peculiarity of these compounds is that for some clathrates the initial matrix–host complex $[MA_4X_2]$ is thermodynamically unstable and does not exist in the system '$MX_{2(\text{solid})}$–$A_{(\text{liquid})}$'. Clathrates (M/A>4) can be synthesized in these systems, but complexes (M/A=4) can not (so-called the contact stabilization of host molecules during clathrate formation [15]).

All clathrates $[M(4\text{-MePy})_4(NCS)_2]{\cdot}0.67(4\text{-MePy})$ (M=Co, Mn, Cd, Cu), decompose instantaneously to $[M(4\text{-MePy})_2(NCS)_2]$. In this series only the copper matrix complex $[Cu(4\text{-MePy})_4(NCS)_2]$ is not exist for himself, others exist as a thermodynamically stable phases. The analogy in reaction mechanism is supported by the compensation dependence (Fig. 1). The kinetic parameters in the series correlate with the length of the metal–ligand bonds inside the coordination spheres of the clathrates

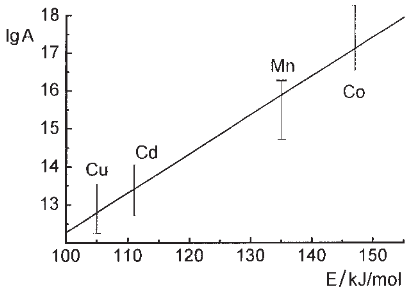

Fig. 1 Kinetics of thermal dissociation of clathrates $[M(4\text{-MePy})_4(NCS)_2]{\cdot}0.67(4\text{-MePy})$ (M=Cu, Cd, Mn, Co)

(L_{Mn-N}=2.34 Å, L_{Cd-N}=2.49 Å, L_{Cu-N}=2.51 Å); we remember that real bonds lengths in reaction zone is different, but hope that their variation: Cu>Cd>Mn – is the same. The experiments show that the existed host complexes [M(4-MePy)$_4$(NCS)$_2$] (*M*=Co, Mn, Cd) also decompose instantaneously to [M(4-MePy)$_2$(NCS)$_2$]. We can conclude that the kinetic stability of clathrates depends mainly upon the stability of the host complex matrix, shaped by the clathrates framework. The change in the length of the metal-ligand bonds explains why [Mn(4-MePy)$_4$(NCS)$_2$] exists as a stable phase and [Cu(4-MePy)$_4$(NCS)$_2$] does not.

The experiments prove that the series of compounds have general regularities, connected not only with the specific stoichiometry of the first step of the reaction (decomposition either to [MA$_4$X$_2$], or to [MA$_2$X$_2$]), but with the mechanism peculiarities. Most likely that such regularities are connected with the similarity in activated complex (transition state) structure, which further can transform in certain compound (thermodynamically stable in real experimental conditions).

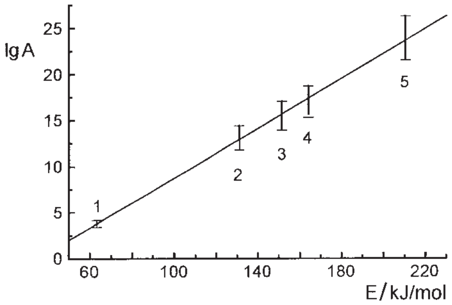

Fig. 2 Kinetics of thermal dissociation of complexes; 1 – [Cd(*p*-tol)$_2$I$_2$]; 2 – [CdAn$_2$(SCN)$_2$]; 3 – [Cd(*m*-tol)$_2$Cl$_2$]; 4 – [Cd(Me-An)$_2$Cl$_2$]; 5 – [CdAn$_2$Cl$_2$]

We have studied the thermal dissociation for series of complexes with aniline and its derivatives [MA$_2$X$_2$] (*M*=Mn, Co, Ni, Cu, Zn, Cd, *A*=NH$_2$C$_6$H$_5$, CH$_3$NHC$_6$H$_5$ and *o*-, *m*-, *p*-NH$_2$C$_6$H$_4$CH$_3$, *X*=Cl, I, 1/2SO$_4$). The compensation dependence was observed for several series of compounds, and several series were iso-enthropy ones. The results are rather interesting for [CdA$_2$X$_2$] complexes (Fig. 2). The linear depedence lg*A* *vs.* *E* exists, although this series of complexes has four different amino-ligands and three different acido-ligands (we can note, that complexes with SO_4^{2-}-acido-ligand do not belong among this series).

Concluding remarks

The chemical reaction progress (during the thermal dissociation) covers the micro-blocks of distorted surface layers (with rate being averaged over originally anisotropic directions). The kinetic investigations of thermal dissociation reactions gives the possibility to obtain the quantitative data of kinetic lability of coordination (as well as inclusion) compounds in series. These data can be interpreted in terms of processes mechanism, if the experimentator keeps at a time in mind both the introduced approximations, and the physicalo-chemical restrictions.

The introduction of these above mentioned approximations is a small price to pay for the creation and advancement of solid state coordination chemistry (with specific reaction within the reaction zone) which can (and must) be every bit as important as the coordination chemistry in solutions.

References

1 V. V. Alekseenko, 'The elemental act of the atoms rearrangement in the solid body. Analytical calculations and computer modeling', Thesis of dissertation, Novosibirsk 1983 (in Russian).

2 Z. Slanina, Teoreticke aspekty fenomenu chemicke isomerie, Praha 1981.

3 N. A. Simakova, Kinetics of the thermal dehydration of $Li_2SO_4H_2O$ with consideration for the heat and mass exchange in the reaction zone, Thesis of dissertation, Novosibirsk 1994 (in Russian).

4 A. I. Ginak, V. A. Dimshits and A. Ya. Rosovskiy, Kinetika i katalis, 30 (1989) 83 (in Russian).

5 V. I. Evdokimov, Chemical sublimation, Moscow, Znanie 1984 (in Russian).

6 N. A. Bogolubov and S. I. Masharov, The vaporization of atom- and magneto-ordered crystals with defects, Novosibirsk, Nauka 1989 (in Russian).

7 G. K. Boreskov, Theoretical problems of the catalysis, Novosibirsk, Nauka 1977 (in Russian).

8 G. Darwin, Phil. Mag., 27 (1914) 675.

9 Yu. I. Vesnin, The secondary structure and properties of crystals, Novosibirsk 1997 (in Russian).

10 A. Adamson, The physical chemistry of surfaces, Moscow, Mir 1979 (Russian translation).

11 G. Benson and K. Yun, The surface energy and surface tension of crystalline solids (in 'Gas–solid interface'), Moscow, Mir 1970 (Russian translation).

12 N. L. Allinger, M. A. Miller et al., J. Amer. Chem. Soc., 89 (1967) 4345.

13 F. Satava and J. Šesták, J. Thermal Anal., 8 (1975) 477.

14 J. Šesták, Thermophysical properties of solids, Academia Prague, 1984.

15 Yu. A. Dyadin and N. V. Kislykh, Mendeleev Commun., 1991, 134.