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QUASI - EQUILIBRIUM THERMOGRAVIMETRY IN COORDINATION CHEMISTRY

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ABSTRACT

The unique possibilities of the thermogravimetry technique under quasi-equilibrium conditions (Q-Derivatograph) have been considered from the study of thermal dissociation reactions of coordination compounds with volatile ligands (water, amines), Anderson's rearrangement,processes of high temperature hydrolysis of aquo-complex compounds, the dehydration and dehydroxylation reactions of minerals of glauconite group.

INTRODUCTION

The traditional thermoanalytical technique, constantly improving during last years, is invariably based on the linear heating rate law. In studing the processes of thermal dissociation, all information obtained concerns the kinetic stability of compounds /1/. Only recently new thermoanalytical equipment (Q-Derivatograph)/2/was created; this equipment allows the investigation of the thermal decomposition reactions to be carried out under quasi-isobaric quasi-isothermal conditions. The reactions with easily established equilibrium occur under quasi-equilibrium conditions: the stabilized decomposition temperature is very close to the equilibrium one ($A_s \rightleftharpoons B_s + C_g$) under specific evolved gas pressure, determined by the type of sample holder (0.01 - 1.0 atm.). The physico-chemical information of this untraditional thermoanalytical method is unique.

The minimum rate of the weight loss g = 0.16 mg/min corresponds to almost equal rates of direct and reverse reactions (difference $\sim 10^{-7}$ mol/sec) under quasi-equilibrium conditions in labyrinth sample holder and almost equal rate constants (for processes of removing water or ammonia). The worse isothermal conditions of the decomposition in uncovered and multi-plate sample holders ($P_{gas} \approx 0.05-0.01$ atm.) are not connected with the worse stabilization of pressure, but with the necessity of the rate constant of reverse reaction being two orders greater, than the

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rate constant of direct reaction.

RESULTS AND DISCUSSION

Thermodynamic Stability Series. Quasi-equilibrium temperature of the decomposition in the labyrinth sample holder is the temperature of the reach of $K_{equil} = 1$. This temperature can be used as measure of the thermodynamic stability in the series of similarly constructed compounds/3/. It is possible to detect the isoequilibrium temperature, using other sample holders ($P_{gas} = 0.2$-0.01 atm.).

The use of the quasi-equilibrium thermogravimetry clearly demonstrates the lack of the connection between the original complex structure (coordinated and uncoordinated water molequles) and the steps of the dehydration process. The dehydration process of EDTA complex compounds (isostructural) $Mg_2L\cdot 9H_2O$, $Mn_2L\cdot 9H_2O$, $MgMnL\cdot 9H_2O$, $MgCdL\cdot 9H_2O$ leads to the different intermediate hydrates, their composition depending also on the pressure of water vapour. The attempt of the detection of the "firmly bound" and "weakly bound" water molequles according to the steps of the thermal dehydration is physico-chemical misconseption/1/.

High Temperature Hydrolysis of Aquo-Complex Compounds. The features of the EDTA chelate dehydration process $[Zn(H_2O)_4][ZnL]\cdot 2H_2O$ depend on the pressure of water vapour; the monohydrate stable to 330°C is obtained only under $P_{H_2O} \approx 1$ atm. High temperature Infra-Red Spectroscopy showed that solid-state hydrolysis takes place under 170-210°C with formation of the hydroxocomplex compound and with EDTA ligand carboxyl proton attachment/1/.

The Detection of Unstable Intermediates. Anderson's rearrangement process was studied:

$$(PyH)_2[PtCl_4] \longrightarrow [PtPy_2Cl_2] + 2HCl \qquad /4/$$

The step-like proceeding of the process with the formation of $(PyH)[PtPyCl_3]$ is observed under linear heating; but this compound does not exist under quasi-equilibrium conditions of the decomposition. The compound $(PyH)[PtPyCl_3]$ is unstable intermediate, formed in accordance with Ostwald's rule of the steps.

Reactions with Irreversible Second Step. The decomposition processes of the complex compounds of transitional metals were studied:

$$[MCl_2(N_2H_4)_2] \rightleftharpoons MCl_2 + 2N_2H_4 \longrightarrow MCl_2 + N_2 + NH_3$$

The dependence of the decomposition temperature on the gas pressure-reaction product (different sample holders) clearly indicates at the presence of the undecomposed molecular hydrazine in a system.

The Synthesis and Investigation of Intermediate Phases. When studing the kinetics of thermal decomposition processes it is necessary to check the investigated reaction to be a single-stage one. The reaction:

$$[NiSO_4(m\text{-}tol)_2] \longrightarrow NiSO_4 + 2\ m\text{-}tol$$

was studied as a model. The amine splitting can take place theoretically through two stages: parallel-consecutive reactions with close temperature intervals. This fact can be unnoticed through the kinetic treatment of the visually "smooth" kinetic curve of the gas evoluation (a flow-gas reactor, sample mass 10 mg;the helium flow rate 80 ccm/min, a conductometric detector, 4 K/min). The intermediate phase $NiSO_4(m\text{-}tol)$ was synthesized under quasi-equilibrium conditions (the labyrinth sample holder). Compounds kinetic stability:

I $[NiSO_4(m\text{-}tol)]$: $E = 148 \pm 6$ kJ, $\lg A = 12.9 \pm 0.6$

II $[NiSO_4(m\text{-}tol)_2]$: $E = 145 \pm 6$ kJ, $\lg A = 18.4 \pm 0.6$

All difference in their kinetic stability is connected with the entropy factor. The decomposition of $[NiSO_4(m\text{-}tol)_2] \rightarrow NiSO_4 + 2\ m\text{-}tol$ can be considered as a single-stage process, since the value $k_{II}/k_I = 10^6$.

The Clathrate Stability. The decomposition of clathrates, formed by Scheffer's complex compounds, $[M(NCS)_2(\gamma\text{-pic})_4]$, M = Co, Ni, Cd; "guest" molecules: γ-picoline, benzene, xylenes/5/ have been studied. From the quasi-equilibrium decomposition temperatures comparison it is evident, that the clathrate formation leads to the noticeable energy gain and to the increasing of the clathrate stability in comparison with the original "host"-complex.

Dehydration and Dehydroxylation of Minerals of Glauconite Group. The method allows the steps of removing molecular-combined water and dehydroxylation to be separated more reliable. The processes of dehydration-rehydration, dehydroxylation-rehydroxylation have been studied. The differential dependence (the weight loss divided to temperature unit, as a function of temperature: $\Delta m/\Delta T = f(T)$ - "temperature rate") was used; this allowed to isolate two-three steps of dehydroxylation/7/.

CONCLUSIONS

The using of the method of thermal analysis under quasi-equilibrium conditions allows to obtain basically new data about the kinetic and thermodynamic features of the studied processes of the thermal dissociation. Its new important possibilities: the detection of the thermodynamic stability series (with the search of the isoequilibrium point), the synthesis of intermediate phases, the detection of unstable intermediates.

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