

## **STUDY OF DEHYDRATION KINETICS OF HETEROPOLY MOLYBDATE AND TUNGSTATE COMPLEXES OF GALLIUM(III)**

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The dehydration processes of heteropoly hexamolybdate and dodecatungstate complexes of gallium were investigated. The kinetics of dehydration were studied in a flow reactor, the obtained activation energy values being 50–107 kJ/mol, and the pre-exponential factor  $10^4$ – $10^{13}$  s<sup>-1</sup>. The nature of the external cation does not influence the dehydration kinetics essentially. The activation energy and pre-exponential factor values increase on transition from the high-hydrated tungstates to the low-hydrated molybdates.

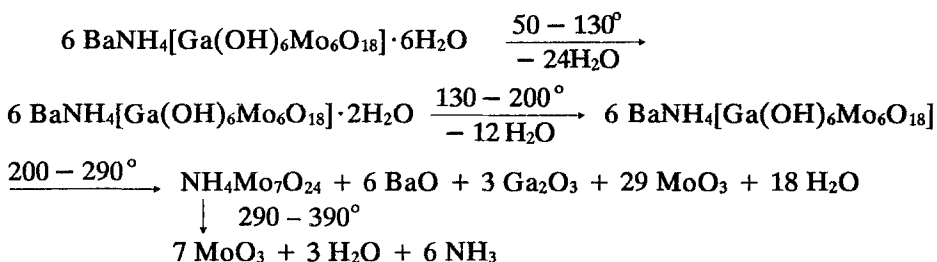
There is considerable interest in heteropoly compounds due to their wide-ranging practical use. Heteropoly molybdate and tungstate complexes of gallium(III) are of great interest as multicomponent metal oxide catalytic systems [1]. The literature information on heteropoly compounds of gallium is limited. An experimental investigation of thermal transformations and kinetics of decomposition processes is therefore of scientific significance and can form the theoretical basis for the preparation of materials with planned properties.

The present paper discusses a study of the kinetics of thermal decomposition of the following octahedrally coordinated complexes:  $\text{CaNH}_4[\text{Ga}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 10\text{H}_2\text{O}$ ;  $\text{SrNH}_4[\text{Ga}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 6\text{H}_2\text{O}$ ;  $\text{BaNH}_4[\text{Ga}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 6\text{H}_2\text{O}$ ;  $\text{BaH}[\text{Ga}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 3\text{H}_2\text{O}$ ; and the tetrahedrally coordinated  $\text{Ca}_2\text{H}[\text{GaW}_{12}\text{O}_{40}] \cdot 22\text{H}_2\text{O}$ ;  $\text{Sr}_2\text{H}[\text{GaW}_{12}\text{O}_{40}] \cdot 20\text{H}_2\text{O}$ ;  $\text{Ba}_2\text{H}[\text{GaW}_{12}\text{O}_{40}] \cdot 16\text{H}_2\text{O}$ ; and  $\text{H}_5[\text{GaW}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O}$ .

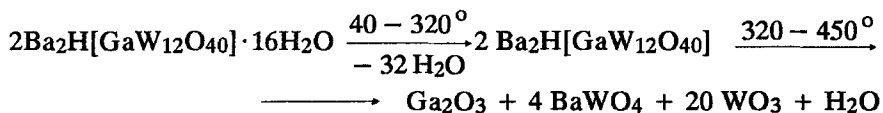
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The syntheses and physico-chemical properties of these compounds are described in [2-5].

Thermoanalytical investigations [5] earlier showed that the thermal decomposition of these hexamolybdates proceeds in several stages, connected with the removal of crystal water, hydroxygroups and ammonia, and decay of the heteropoly anion. The character of the thermal behaviour of the compounds of this structural type is identical. Their thermolysis can be illustrated by the following scheme for the barium-ammonium salt:



The thermal transformations of the dodecatungstates differ from those of the molybdates. Their dehydration begins at 40-50° and occurs in one stage without a distinct division into steps. The thermolysis proceeds according to the scheme:



An attempt was earlier made [5] to find a correlation between the thermal stability of these compounds and the radius of the cation in the outer sphere. It was concluded that, although the nature of the outer sphere cation influences the character of the dehydration, the stability of the heteropoly anion itself plays the determining role in the thermal stability. It was noted that the thermal stability of the molybdate complexes was less than that of the tungstate compounds, which are characterized by the greater strength of the W - O bond.

To study the kinetics of the dehydration processes, we used a flow reactor [6]. The sample (10 mg) was heated linearly at a rate of 4-5 deg/min, the helium flow through the sample was 60 cm<sup>3</sup>/min, and the gas evolution curve was recorded with a conductometric detector. Such an experimental set-up

allows the avoidance of diffusional braking of the process and the reduction of concentration and temperature gradients in the sample. With a flow of helium through a sample placed on a porous substrate, the conditions of decomposition are similar to the conditions of dynamic vacuum. This prevents a contribution of a reverse reaction (the pressure of isolated gas is lower than 0.1 torr).

To process the gas evolution kinetic curves, we used the integral method of Šestak and Šatava with the computer program TA IV [6]. After computing 13 kinetic equations (diffusion, nucleus formation, nucleus growth and chemical reaction on the interphase boundary), we selected the equation best describing the process with linearity of the function  $\lg g(\alpha)$  vs.  $1/T$ . For the compounds studied, the best equation over the conversion range  $\alpha \approx 5$ –50% was the equation of a shrinking sphere  $[1 - (1-\alpha)^{1/3}]$  (chemical reaction on the interphase boundary).

The calculated activation energy and pre-exponential factor values are given in Table 1. For the molybdate complexes, the dehydration kinetics was investigated only for the first stage of water removal. We did not calculate the kinetic parameters for  $H_5[GaW_{12}O_{40}] \cdot 14H_2O$  and  $CaNH_4[Ga(OH)_6Mo_6O_{18}] \cdot 10H_2O$  because of the inseparability of the dehydration steps.

Table 1 Kinetic parameters of the dehydration reactions

Compounds	$E_a$ , kJ/mol	$\lg Z$	$t_{init}$ , °C
$SrNH_4[Ga(OH)_6Mo_6O_{18}] \cdot 6H_2O$	102.4	11.8	58
$BaNH_4[Ga(OH)_6Mo_6O_{18}] \cdot 6H_2O$	104.1	13.6	29
$BaH[Ga(OH)_6Mo_6O_{18}] \cdot 3H_2O$	107.4	11.4	92
$Ca_2H[GaW_{12}O_{40}] \cdot 22H_2O$	80.7	9.9	22
$Sr_2H[GaW_{12}O_{40}] \cdot 20H_2O$	50.6	4.4	35
$Ba_2H[GaW_{12}O_{40}] \cdot 16H_2O$	52.7	5.1	29

## Discussion

The activation energy values fall within the range 50–107 kJ/mol (Table 1). This indicates the removal of water of crystallohydrate type [7]. On transition from the high-hydrated tungstate complexes to the low-hydrated molybdate compounds, the activation energy and pre-exponential

factor increase. This is in accord with the structural ideas about crystallohydrates of such a type. The low values of the kinetic parameters are caused by the removal mainly of weakly-combined "tunnel" water from the space between the anions. Its molecules are kinetically mobile. The distances  $O_{H_2O} \dots O_{GPA}$  are 2.9–3.4 Å [8–10] in such a compound. The higher parameters for the molybdate complexes are obviously due to the removal of kinetically stable molecules of water coordinated to the external cations, the cation - water bond lengths in these compounds being 2.3–2.5 Å [11–13]. This indicates the greater strength of the water bonds in the low-hydrated complexes. The calculated value of the activation energy here seems to be determined by the energetics of breaking of the water-cation bonds.

The pre-exponential factor values for the compounds studied lie in the interval  $10^4$ – $10^{13}$  s<sup>-1</sup> (Table 1). Pre-exponential factor values  $A < 10^{13}$  s<sup>-1</sup> demonstrate the considerable regularity of the transition state in the initial step of dehydration in comparison with the original crystallohydrate [6, 14]. This conclusion is confirmed by the work of Beyker [15], in which the change in the parameters of the elementary cell was investigated radiographically when heteropoly compounds were heated to 40°; it is also in accord with the findings of Chuvaev and Bahchisaraitseva [16, 17]. The removal of crystallohydrate water was found to cause a contraction of the

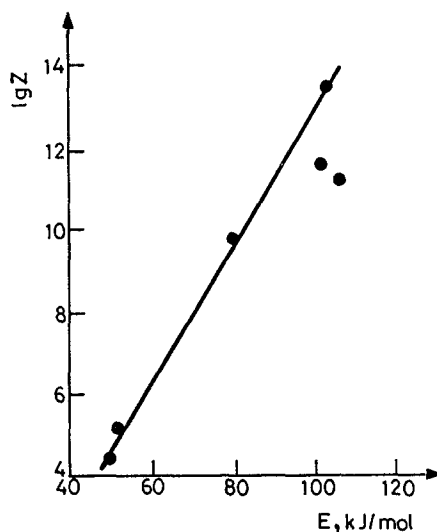


Fig. 1 Compensation effect  $\lg A = aE + b$  in dehydration reactions

heteropoly compounds, a change in the system of hydrogen-bonds, and as a result the regulation of the structure.

The data obtained reveal that the nature of the external cation does not influence the dehydration kinetics essentially. Although the radius of the external cation influences the water content of the salt structure and the dehydration character, it does not influence the destruction of the heteropoly complex. Investigations of molybdate gallates by methods of radiophase analysis and IR-spectroscopy [18, 19] showed that the structural changes of the heteropoly anion do not occur during the loss of crystallohydrate water. As a rule, the removal of crystallohydrate water from many dodecaungstates does not lead to their decomposition or structural change either. Thus, the conservation of the structure indicates the lack of influence of the external cation on the destruction of the heteropoly complex and, consequently, on the thermal stability. The latter is obviously conditioned by the strength of the anion itself.

The compensation relationship  $\lg A = aE + b$  is not observed for all the compounds studied (Fig. 1). The values of  $\lg A$  and  $E$  for  $\text{SrNH}_4[\text{Ga}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 6\text{H}_2\text{O}$  and for  $\text{BaH}[\text{Ga}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 3\text{H}_2\text{O}$  are not subject to the given dependence.

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**Zusammenfassung** — Es wurde der Dehydratierungsprozeß der Heteropolyhexamolybdat- und Dodecawolframat-Komplexe von Gallium untersucht. Die Kinetik der Dehydratierung wurde in einem Durchflußreaktor untersucht, die erhaltenen Werte für die Aktivierungsenergie und den präexponentiellen Faktor betragen 50-107 kJ/mol bzw.  $10^4$ - $10^{13}$  s<sup>-1</sup>. Die Kinetik der Dehydratierung wird durch externe Kationen nicht wesentlich beeinflußt. Aktivierungsenergie und präexponentieller Faktor steigen beim Übergang vom hochhydratierten Wolframat zum niederhydratierten Molybdat.