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 10⁷–10¹³ s⁻¹. 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: CaNH₄[Ga(OH)₆Mo₆O₄₈]⋅10H₂O; SrNH₄[Ga(OH)₆Mo₆O₄₈]⋅6H₂O; BaNH₄[Ga(OH)₆Mo₆O₄₈]⋅6H₂O; BaH[Ga(OH)₆Mo₆O₄₈]⋅3H₂O; and the tetrahedrally coordinated Ca₂H[GaW₁₂O₄₀]⋅22H₂O; Sr₂H[GaW₁₂O₄₀]⋅20H₂O; Ba₂H[GaW₁₂O₄₀]⋅16H₂O; and H₃[GaW₁₂O₄₀]⋅14H₂O.
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:

$$\begin{align*}
6 \text{BaNH}_4[\text{Ga(OH)}_6\text{Mo}_6\text{O}_{18}] \cdot 6\text{H}_2\text{O} & \xrightarrow{50-130^\circ} 6 \text{BaNH}_4[\text{Ga(OH)}_6\text{Mo}_6\text{O}_{18}] \cdot 4\text{H}_2\text{O} \\
6 \text{BaNH}_4[\text{Ga(OH)}_6\text{Mo}_6\text{O}_{18}] \cdot 2\text{H}_2\text{O} & \xrightarrow{130-200^\circ} 6 \text{BaNH}_4[\text{Ga(OH)}_6\text{Mo}_6\text{O}_{18}] \\
\text{NH}_4\text{Mo}_7\text{O}_{24} + 6 \text{BaO} + 3 \text{Ga}_2\text{O}_3 + 29 \text{MoO}_3 + 18\text{H}_2\text{O} & \xrightarrow{200-290^\circ} 7 \text{MoO}_3 + 3\text{H}_2\text{O} + 6\text{NH}_3
\end{align*}$$

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:

$$\begin{align*}
2\text{Ba}_2\text{H}[\text{GaW}_{12}\text{O}_{40}] \cdot 16\text{H}_2\text{O} & \xrightarrow{40-320^\circ} 2\text{Ba}_2\text{H}[\text{GaW}_{12}\text{O}_{40}] \\
\text{Ga}_2\text{O}_3 + 4\text{BaWO}_4 + 20\text{WO}_3 + \text{H}_2\text{O} & \xrightarrow{320-450^\circ}
\end{align*}$$

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$^3$/min, and the gas evolution curve was recorded with a conductometric detector. Such an experimental set-up