Study on the kinetics of the isothermal decomposition of selenites from IIIB group of the periodic system

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Abstract

Both the thermal stability and the kinetics of the isothermal decompositions of the selenites of aluminium, gallium and indium have been studied. A relationship between the activation energy of the process and the radius of cations was found. Such a relationship is believed to result from the effect of counter-polarization of the selenite anion, that depends on the cation nature. The negative values of the activation entropy changes show that the active complex has a more complicated structure than the starting reactant. The increase of the observed absolute values of the activation entropy changes from indium to aluminium selenite also indicates that the structure of the active complex improves with the decrease of cation radius. The values of the steric factor calculated from the Arrhenius equation are significantly lower than unity which means that the isothermal decomposition of selenites from IIIB group of the periodic system belongs to the so-called ''slow'' reactions. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Synthesis and studies of the properties of selenites has been done mostly because some of these compounds are ferroelectrics whereas others possess anti-ferroelectric properties [1]. Moreover, selenites convert to selenides on heating under reductive conditions and this way novel semi-conducting and dielectric materials have been obtained [2]. In this connection, the synthesis and characterization of selenites of aluminium, gallium and indium (which are not available in nature) is of certain interest from both the theoretical and practical point of view. Methods for preparation, as well as some structural characteristics and physicochemical constants have been described

by other authors [1–6]. On heating at temperatures over 723 K, these selenites are known to undergo thermal decomposition as follows:

$$Me_2(SeO_3)_3 \rightarrow Me_2O_3 + 3SeO_2$$
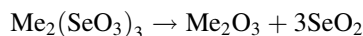
Under these conditions, SeO_2 is obtained as a sublimate [2]. No data, however, concerning the kinetics of this process is available. Therefore, the aims of the present work were to study the thermal stabilities of selenites of aluminium, gallium and indium and to evaluate the basic kinetic parameters of the decomposition process as well as the trends in properties.

2. Experimental

The procedures of the synthesis of $Al_2(SeO_3)_3$, $Ga_2(SeO_3)_3$ and $In_2(SeO_3)_3$ have been described in

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details previously [4–6]. The samples were characterized by chemical, X-ray diffraction and TGA/DTA analyses. The time dependence of the decomposition of the selenites at isothermal conditions was studied by thermogravimetry. Continuous weighing of 0.1–0.2 g samples with particle size below 0.1 mm on an analytical balance (accuracy of ± 0.0001 g) was employed. The samples were heated in a vertical furnace with electronic thermoregulator (type ESPA-4, Bulgaria). After reaching the selected temperature, the furnace was lifted up to the sample, which is contained in a small quartz basket. The latter was attached to the balance pan by means of a platinum wire. The temperatures of the sample and in the furnace were measured separately by two thermocouples. The sample was found to reach the selected temperature after an induction period of 30 s. For the calculations, this value was subtracted from the total time necessary for reaching certain degree of decomposition of the reagent. The measurements were carried out in air in the temperature range of 723 to 973 ± 1 K and the sample mass was monitored at certain time intervals. According to the data from DTA analysis and some authors [1–3], selenites decompose without melting in the temperature region studied.

The topokinetical Avrami–Erofeev equation [7–9] was employed to characterize the kinetics of decomposition of selenites:

$$\alpha = 1 - \exp(-kt^n), \tag{1}$$

where α is the fraction of the selenite decomposed at the time t, k the apparent rate constant and n is a parameter whose value depends on the nature of the specific process (which determines the formation and the grow of the initial nuclei and their geometric shape).

After twofold logarithmic procedure, a linear equation is obtained:

$$\ln[-\ln(1 - \alpha)] = \ln k + n \ln t \tag{2}$$

The exponent n was determined from the slope of the straight line, representing the function $\ln[-\ln(1 - \alpha)] = f(\ln t)$. The apparent rate constant k was obtained from the cut-off on the ordinate axis. The "true" rate constant K can be calculated from the

equation proposed by Sakhovitch [7,9]:

$$K = nk^{1/n} \tag{3}$$

From the plot $\ln K = f(1/T)$ obtained from the values of the "true" rate constants at different temperatures, the apparent activation energy E_A and pre-exponential factor A in the Arrhenius equation were obtained, according to the next equation [10,11]:

$$\ln K = \ln A - E_A/RT \tag{4}$$

The least square method was used for the calculations, based on Eqs. (2) and (4).

Further, the change of the entropy of activation ΔS^* [J mol^{-1} K^{-1}] and the corresponding steric factor $P = \exp(\Delta S^*/R)$ were calculated from the fundamental equation in the theory of activated complexes (transition state) [10,11]:

$$K = \frac{\chi e k_B T}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-E_A}{RT}\right), \tag{5}$$

where χ is a transmission coefficient which is unity for monomolecular reactions, k_B the Boltzmann constant, h the corresponding Plank constant and $e = 2.7183$ is the Neper number.

From the well-known thermodynamic functions [10]:

$$\Delta H^* = E - RT \tag{6}$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{7}$$

the corresponding changes of both the enthalpy ΔH^* and free energy ΔG^* of activation (which are associated with the formation of the activated complex from the starting reagents) were obtained. The analysis as well as the comparison of these parameters led to a reliable estimation, concerning the kinetics of topochemical decomposition of selenites.

3. Results and discussion

The experiments on the stability and the rate of the isothermal decomposition of selenites from IIIB group of the periodic system in the temperature interval from 723 to 973 K showed significant differences with respect to the elements concerned. Fig. 1 shows the kinetic curves representing the time dependence of the percentage of selenite decomposed at $T = 823$ K.
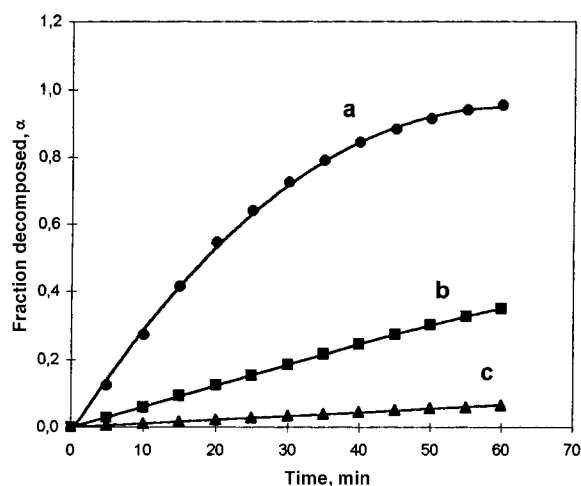
Fig. 1. Kinetic curves of the isothermal decomposition of selenites at 823 K: (a) $Al_2(SeO_3)_3$; (b) $Ga_2(SeO_3)_3$; (c) $In_2(SeO_3)_3$.

The fastest decomposition was observed for $Al_2(SeO_3)_3$ and the slowest — for $In_2(SeO_3)_3$. This indicates that $Al_2(SeO_3)_3$ has the lowest kinetic stability and $In_2(SeO_3)_3$ the highest one. Obviously, significant differences in the values of the parameters (n and k) characterizing the kinetics of isothermal decomposition of selenites should be expected.

Table 1 showed the values of the parameter n and apparent rate constant k in the Avrami–Erofeev equation.

As seen from Table 1, the values of the parameter n increased regularly with the temperature. On the other hand, at a given temperature, the same parameter decreased from $Al_2(SeO_3)_3$ towards $In_2(SeO_3)_3$. It has been reported [9] that the value of the parameter

n depends on the kinetic characteristics, associated with the formation of nuclei for the new phase, as well as their geometry [7,9]. According to literature [7,9], if n-values are lower than unity then the thermal decomposition is most probably diffusion controlled, i.e. the surface layer of the newly formed phase prevents the diffusion of SeO_2 (g) released. In the present case, however, this explanation cannot be accepted, since the value of the Pilling–Bedwordt criterion $\Delta = M_B \rho_A / M_A \rho_B$ [12] (representing the ratio between the molar volumes of the product and the reactant) was less than unity. In such a case, the oxide phase formed is believed to be porous and cannot entirely "block" the selenite nucleus. As a result, no significant obstacle, preventing the SeO_2 diffusion should exist. The observed increase in the n-values with the increase of temperature was possibly due to the change in nuclei shape as a function of their formation rate. This assumption is based on one earlier reports [13], stating that a temperature increase gives a stronger effect on the polarization interactions between the cation and the selenite anion. These polarization interactions are most pronounced with the small and hardly distortable Al^{3+} and least pronounced with the large and easily distortable In^{3+}. Thus, the corresponding bond strength decreases from $Al_2(SeO_3)_3$ to $In_2(SeO_3)_3$, due to the increased covalent character of the bond.

With the values of K calculated using Eq. (3), a graphic representation of $\ln K$ versus $1/T$ is given on Fig. 2.

The values of E_A and A were determined using the Arrhenius Eq. (4). The kinetic parameters of the thermal decomposition of the selenites studied are summarized in Table 2.

Table 1
Values of the parameter n and the apparent rate constant k of the thermal decomposition for the compounds studied at different temperatures

Temperature (K)	$Al_2(SeO_3)_3$		$Ga_2(SeO_3)_3$		$In_2(SeO_3)_3$	
	n	k (min^{-1})	n	k (min^{-1})	n	k (min^{-1})
723	0.60	3.07×10^{-2}	0.53	1.17×10^{-2}		
773	0.86	2.28×10^{-2}	0.78	3.73×10^{-2}		
823	1.27	1.71×10^{-2}	1.08	5.20×10^{-3}	1.03	1.00×10^{-3}
873	1.39	6.61×10^{-2}	1.16	4.35×10^{-2}	1.05	8.02×10^{-3}
923					1.00	5.70×10^{-2}
973					1.45	8.41×10^{-2}
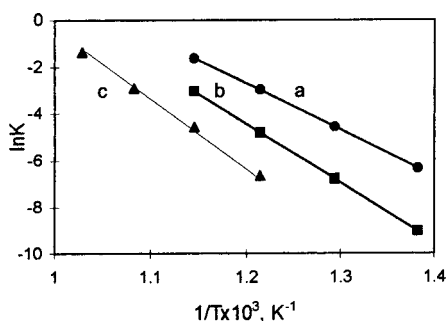
Fig. 2. Arrhenius plot of the thermal decomposition of: (a) $Al_2(SeO_3)_3$; (b) $Ga_2(SeO_3)_3$; (c) $In_2(SeO_3)_3$.

The most significant result is that the thermal stability of the selenites sharply decreases with the decrease of cation radius (as expressed by the correspondingly lower activation energy of thermal decomposition). This is believed to be due to the counter-polarization of SeO_3^{2-} anion caused by its cation [13] and this effect is stronger with smaller cations. As a result, the statistically closest oxygen ion would be affected by the positive charge of the cation and its electron density would undergo change in polarization, directed towards the source of positive charge. Furthermore, the decrease of the electron density located between selenium and the counter-polarized oxygen ions results in weaker covalent Se–O bonds and lower thermal stability of the selenite. The strongest effect of counter-polarization was observed with the small Al^{3+} cation and the weakest one — with the large In^{3+} [14].

Similar trend has been observed with the thermal stability of other inorganic compounds such as hydroxides, carbonates and sulfates [12]. For instance, a study of the kinetics of thermal decomposition of mellitic acid salts [15] has established a correlation between the cation radius and the pre-exponential factor of the Arrhenius equation. A linear relationship between the activation energy of thermal decomposition of mellitic and oxalic acid salts and the enthalpy of their formation was also found [15]. Dollimore, et al. have also noted that the decomposition temperature of oxalates [16] and orthophosphates [17] is directly connected with the cation radius. Other authors [18,19] studied the activation energies and the reaction enthalpies of the α-$AgMO_2$ decomposition as a function of the M^{3+} ion. The explanation of these observations, however, was not based on the counter-polarization effect in the anions.

The second essential result from the present study is that the entropy change ΔS^* for the formation of the activated complex from the starting reactant, unlike the activation energy E_A, is always negative and decreases from $Al_2(SeO_3)_3$ to $In_2(SeO_3)_3$. The negative values suggest that the degree of structural "complexity" (arrangement, "organization") of the activated complex was higher than that of the starting selenite. The greatest absolute value of entropy change was observed with $Al_2(SeO_3)_3$ and the smallest one with $In_2(SeO_3)_3$, which means that the thermal decomposition of the former was associated with the most substantial rearrangement in the structure, while this rearrangement occurred in lower degree with the latter. This indirectly confirmed the stronger counter-polarization effect caused by Al^{3+} as compared to Ga^{3+} and In^{3+} cations.

The third fact that should be considered is the significantly lower than unity value of the steric (entropy) factor P. This means that the thermal decomposition of selenites studied belongs to the so-called "slow" reactions [10,11]. The increase of the value of

Table 2
Kinetic characteristics of the thermal decomposition of selenites[a]

Parameters	$Al_2(SeO_3)_3$	$Ga_2(SeO_3)_3$	$In_2(SeO_3)_3$
Cation radius (Å)	0.50	0.62	0.92
E_A (kJ mol^{-1})	163.8	209.2	237.5
A (min^{-1})	1.23×10^9	1.58×10^{11}	1.48×10^{12}
ΔS^* (J mol^{-1} K^{-1})	-120.6	-80.2	-62.7
P	5.01×10^{-7}	6.43×10^{-5}	5.29×10^{-4}
ΔH^* (kJ mol^{-1})	157.8	203.2	230.7
ΔG^* (kJ mol^{-1})	245.0	261.2	282.3

[a] The values of ΔS^*, ΔH^* and ΔG^* for aluminium and galium selenites were calculated at 723 K, while that of indium selenite at 823 K.

steric factor from the aluminium to indium selenite, however, cannot compensate for the higher values of activation energy and, therefore, the rate of thermal decomposition decreases in the same direction. Obviously, the entropy component cannot exceed the internal energy involved in the rearrangement of the molecule from the starting material to its transition state.

It may be concluded that the thermal decomposition rate of selenites from IIIB group of the periodic system is directly connected with the degree of counter-polarization of SeO_3^{2-}, which in turn is determined by the size of the cations and their electron polarizability.

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