

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

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Abstract

The thermal stability and kinetics of isothermal decomposition of the selenites of germanium, tin and lead was studied. A dependence between the process activation energy and the radius and electron polarizability of the cations was observed. It was explained with the different degree of the effect of counterpolarization of the selenite anion. The negative value of the change of entropy of activation showed that the active complex is more complicated formation than the reagent. The higher absolute value of the change of entropy measured for the formation of the active complex $\text{Ge}(\text{SeO}_3)_2$ compared to that for $\text{Sn}(\text{SeO}_3)_2$ shows that the degree of rearrangement (necessary changes) of the initial crystalline structure increases with the decrease of cation radius. The isothermal decomposition of the selenites from IVB group of the periodic system was considered to be ‘slow’ reaction due to the significantly lower than unity values of the steric factor.

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1. Introduction

The thorough review of Verma [1] provided information about the synthesis, structure and thermal behavior of all the known selenites. However, the kinetics of their decomposition under heating had not been discussed obviously due to the lack systematic studies in this field. In our previous work [2], the basic parameters characterizing the kinetics of isothermal decomposition of Al, Ga and In selenites were presented and in [3]—these of Sb and Bi selenites. Of course, the reasons for the relationships observed were also discussed. The present paper extends this information with data about some selenites from the IVB group (Ge, Sn, Pb). The interest towards these selenites is stipulated by the fact that they can be transformed into selenides with valuable semi-conductor properties by heating in reduction medium [4]. Besides, some of these selenites are ferroelectrics and others, antiferroelectrics. For instance, PbSeO_3 is used for production of IR detectors and sensitive photoresistors [5]. In this respect, the synthesis and characterization of the germanium, tin and lead selenites is of both theoretical and

practical interest. From these selenites, only lead selenite can be found in nature as molibdomenite mineral [6]. The synthesis of these selenites, as well as some of their structure characteristics and physicochemical constants have been discussed by a number of authors [1,4,5,7–12]. While the four-valent germanium and tin selenites are stable compounds, the stable selenite of lead is PbSeO_3 since, as it is well known for sub-group IVB, the stability of the compounds with the highest oxidation decreases with the increase of the atomic weight [13]. It is also known that $\text{Sn}(\text{SeO}_3)_2$ exists in two crystalline forms: α and β [4] while the other two selenites have only one modification [5–7]. Both $\text{Ge}(\text{SeO}_3)_2$ and $\text{Sn}(\text{SeO}_3)_2$ thermally dissociate at temperatures above 723 K without melting and form the corresponding oxide and SeO_2 . The latter sublimates at these temperatures [1,4–7]. Two endothermic effects have been reported in the DTA curves of PbSeO_3 [1]: one at 948 K (corresponding to fusion of the salt) and a less defined one at 1063–1103 K indicating the dissociation of PbSeO_3 with evolution of SeO_2 and PbO . Further mass loss up to 1273 K is attributed to the evaporation of PbO .

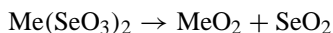
The aim of the present work is to study the thermal stability of germanium, tin and lead selenites and find the basic kinetic parameters characterizing their thermal decomposition, as well as interpretation of the dependencies observed.

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2. Experimental

The compounds studied $\text{Ge}(\text{SeO}_3)_2$, $\text{Sn}(\text{SeO}_3)_2$ and PbSeO_3 were prepared by methods described earlier [8–10]. According to the data obtained from derivatographic thermal analysis and chemical analysis, the decomposition of selenites proceeds according to the following scheme:



The decomposition takes place in static air medium and without changes in Me and Se oxidation degree. SeO_2 sublimates at decomposition temperature ($T = 588 \text{ K}$) while the remaining MeO_2 was found to be amorphous according to X-ray analysis.

The dependence of the degree of decomposition α of the selenite on time at certain temperature was measured by a method described in [2]. The kinetics of isothermal decomposition of the selenites was characterized using the generalized equation of Avrami–Erofeev [14–17]:

$$\alpha = 1 - \exp(-kt^n) \quad (1)$$

where α is the fraction of the selenite decomposed at time t , k the apparent rate constant and n the dimensionless parameter with a value depending on process conditions, form of nucleation centers for the new solid phase and the way of their growth. Since the parameter n changes with temperature [18,19], then the dimension of k would be min^{-1} . For convenience, Sakhovitch [15,16,20] suggested a substitution for the following mathematical operations:

$$K = nk^{1/n} \quad (2)$$

where K is the ‘true’ rate constant with dimension (min^{-1}). The combination of Eqs. (1) and (2) gives [21–23]:

$$\alpha = 1 - \exp\left[-\left(\frac{Kt}{n}\right)^n\right] \quad (3)$$

The linear form of the equation of Avrami–Erofeev can be obtained by taking twice the logarithm of Eq. (3):

$$\ln[-\ln(1 - \alpha)] = n \ln\left(\frac{K}{n}\right) + n \ln t \quad (4)$$

The value of n can be calculated from the slope of the straight line and the ‘true’ rate constant K —from the cut-off on the ordinate axis. This equation was successfully used for studies not only on the kinetics of thermal decomposition of a number of compounds [24–30], dehydration of salts [31,32], phase and polymorphous transitions [33–36], solution [37–39] but also for kinetics of adsorption of ions from solutions onto various adsorbents [21–23]. In some cases, Eq. (3) gives even better results than the kinetic equations for shrinking cylinder, contracting sphere, etc. [36,38,39].

Using the linear form of Arrhenius equation [41,42]:

$$\ln K = \ln A - \frac{E_A}{RT} \quad (5)$$

the values of the activation energy E_A (kJ mol^{-1}) of selenites thermal decomposition and pre-exponential factor A (min^{-1}) in Arrhenius equation can be calculated.

Further, the change of entropy of activation ΔS^\ddagger ($\text{J mol}^{-1} \text{ K}^{-1}$) and the corresponding steric factor $P = \exp(\Delta S^\ddagger/R)$ were calculated from the fundamental equation of the theory of activated complexes (transition state) [40,41]:

$$K = \frac{\chi e k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{E_A}{RT}\right) \quad (6)$$

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

From the well known thermodynamic functions [40]:

$$\Delta H^\ddagger = E_A - RT \quad (7)$$

and

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (8)$$

the corresponding changes of both enthalpy ΔH^\ddagger and free energy ΔG^\ddagger of activation (which are associated with the formation of the activated complex from the initial reagents) were obtained.

All experimental data were processed by the least squares method at correlation coefficient values $R^2 \geq 0.9650$.

3. Results and discussion

The thermal stability and kinetics of decomposition of selenites was studied within the temperature interval 723–1173 K. Since the various selenites have quite different thermal stability, Fig. 1 shows the kinetic curves of decomposition only for the temperatures at which experiments were carried out.

As can be seen from Fig. 1, the degree of selenites decomposition was from 0 to 90% within a 150 K interval and this interval showed a tendency to shift to higher temperatures in the order from $\text{Ge}(\text{SeO}_3)_2$ to PbSeO_3 . It means that the

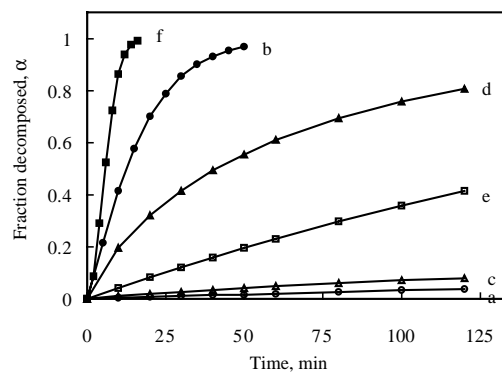


Fig. 1. Kinetic curves of isothermal decomposition of $\text{Ge}(\text{SeO}_3)_2$: (a) 723, (b) 873; $\text{Sn}(\text{SeO}_3)_2$: (c) 773, (d) 873; PbSeO_3 : (e) 1023, (f) 1173 K.

Table 1
Dependence of the values of parameter n and 'true' rate constant K on temperature and nature of selenites

Temperature (K)	Ge(SeO ₃) ₂		Sn(SeO ₃) ₂	
	n	K (min ⁻¹)	n	K (min ⁻¹)
723	0.98	3.02×10^{-4}		
773	1.10	2.32×10^{-3}	0.79	2.86×10^{-4}
823	1.12	1.39×10^{-2}	0.80	2.12×10^{-3}
873	1.16	6.79×10^{-2}	0.81	1.25×10^{-2}
923			0.83	6.02×10^{-2}

thermal stability of these selenites increased in the same direction. Besides, contrary to Ge(SeO₃)₂ and Sn(SeO₃)₂, the decomposition of PbSeO₃ takes place in melt. It means that the strength of the bond Pb–O–Se is quite higher than that of Ge–O–Se or Sn–O–Se. Obviously, the effect of counterpolarization of the selenite anion decreases with the increase of cation radius while its thermal stability increases. Therefore, the decomposition of PbSeO₃ does not begin until it is melted. Since the mechanisms of substance decomposition in solid state and in melt are different, the discussion in our further kinetic studies will be limited only to germanium and tin selenites. Here, the values of the 'true' rate constant calculated from Eq. (4) at these temperatures can be used as quantitative estimate. For comparison, Table 1 presents the values of parameter n and 'true' rate constant K for the selenites studied.

It should be noted that the values of n and K slightly increase with temperature and decrease from Ge(SeO₃)₂ to Sn(SeO₃)₂. The parameter n is known to depend on temperature, form of the nuclei for the new phase and their way of growth [21,23,42]. Values lower than unity are usually interpreted as an evidence that a diffusion controlled reaction took place while values higher than unity means that chemically controlled reaction occurred [28–30]. As can be seen from Table 1, the values of n for Sn(SeO₃)₂ were lower than unity. Probably, the higher density of the newly formed SnO₂ phase limits the diffusion of released SeO₂. This conclusion was confirmed also by the fact that n did not depend on temperature. The values of n for Ge(SeO₃)₂ change within a narrow range remaining close to unity. In this case the thermal decomposition of Ge(SeO₃)₂ took place as a reaction of first or close to first order. May be, the newly formed GeO₂ phase did not limit the diffusion of released SeO₂.

Based on the values of K calculated and the linear form of the Arrhenius equation, the activation energy of the process E_A and pre-exponential factor A can be calculated. Fig. 2 presents an Arrhenius plot of the thermal decomposition of germanium and tin selenites.

As can be seen from the figure, the slope of the curves increased from Ge(SeO₃)₂ to Sn(SeO₃)₂ which means that the activation energy would increase by the same sequence. The differences observed in the decomposition kinetics of the selenites were considered to be due to their different cation radii r_{cat} [43] and electron polarizability ϵ [44]. It

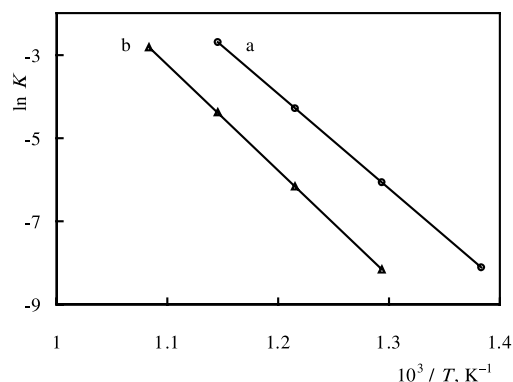


Fig. 2. Arrhenius plot of the thermal decomposition of: (a) Ge(SeO₃)₂ and (b) Sn(SeO₃)₂.

leads to different counterpolarizations of the selenite anions and, respectively, changes of the energy and strength of the Se–O bonds in the selenite, as it has been observed for other salts containing oxoanion [13]. In this connection, the values of the parameters calculated according to Eqs. (5)–(8), the radii and electron polarizabilities of the cations are presented in Table 2 for comparison.

The values of the activation energy and pre-exponential factor in the Arrhenius equation increased from Ge(SeO₃)₂ to Sn(SeO₃)₂, as well as cation radii and electron polarizabilities. The smaller sized Ge⁴⁺ cation polarizes to smaller extent. Therefore, the effect of counterpolarization of the oxoanion oxygen atoms bound to it should be higher. The decrease of the electron density between the selenium atom and the oxygen atom affected by the Ge⁴⁺ cation weakens the Se–O bond which results in lower thermal stability of Ge(SeO₃)₂ compared to the other selenites studied. With the increase of cation radius and, respectively, its electron polarizability, the effect of counterpolarization of SeO₃²⁻ anion was weaker and the thermal stability of the selenite increased. The highest thermal stability was observed for PbSeO₃ because the large sized Pb²⁺ cation can easily be polarized to induce the lowest counterpolarization of the SeO₃²⁻ anion. This conclusion was confirmed also by the fact that Ge(SeO₃)₂ and Sn(SeO₃)₂ decomposed without

Table 2
Kinetic characteristics of the thermal decomposition of selenites^a

Parameters	Ge(SeO ₃) ₂	Sn(SeO ₃) ₂
r_{cat} (Å)	0.53	0.71
ϵ (Å ³)	1.0	3.4
R^2	0.9723	0.9688
E_A (kJ mol ⁻¹)	189	212
A (min ⁻¹)	1.47×10^{10}	5.66×10^{10}
ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	-100.7	-90.1
P	5.49×10^{-6}	1.97×10^{-5}
ΔH^\ddagger (kJ mol ⁻¹)	183	206
ΔG^\ddagger (kJ mol ⁻¹)	256	276

^a The values of ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger were calculated at the lowest decomposition temperature for the corresponding selenite.

melting while PbSeO_3 began to decompose only after melting. The strength of the bonds in the molecule is so high that much higher temperature was necessary to break them. Similar tendency was observed for the selenites from groups IIIB and VB of the periodic system [2,3] as well as for a number of other oxocompounds of the same type [13,24,45–50]. In an attempt to explain the dependencies observed, Belkova et al. [24,47] introduced a new quantity, ionic potential φ representing the ratio of cation charge z to its radius ($\varphi = z/r$). They reported that the higher the value of φ , the lower is the activation energy of decomposition of perchlorates and that this dependence is non-linear and stronger at low values of φ .

In this connection, our investigations clearly indicated the relationship between the thermal stability and decomposition kinetics of these selenites and their cation radii. It was found that the thermal stability increases and decomposition rate decreases from top to bottom of the group and from right to left of the period in the periodic table, i.e. with the increase of cation radius. Further, Ag_2SeO_3 and PbSeO_3 were found to have the highest thermal stability and they begin to decompose at the highest temperature, compared to the other selenites. It means that the Se–O bond in these compounds is very strong and higher temperature (energy) is required to break this bond. The reason for the tendency observed was considered to be the effect of counterpolarization of the oxoanion—its degree is determined by cation radius and corresponding polarizability. It is well known [13] that the carbonates of alkali-earth metals have lower thermal stability than that of alkali metals and the activation energy of thermal dissociation of BaCO_3 and BaSO_4 is higher than that of MgCO_3 and MgSO_4 , respectively. These experimental data were also explained with the effect of oxoanion counterpolarization induced by cations with different radii and polarizabilities. Nevertheless, the data from DTA analysis and isothermal kinetics of decomposition showed that decomposition temperature tends to increase from $\text{Ge}(\text{SeO}_3)_2$ to PbSeO_3 . Besides, the fact that Ag_2SeO_3 and PbSeO_3 begin to decompose only when melted proves that at higher cation radii ($r_{\text{Ag}^+} = 1.26 \text{ \AA}$ and $r_{\text{Pb}^{2+}} = 1.21 \text{ \AA}$) the thermal stability of selenites is very high and the energy necessary to break the bonds is also higher. Vice versa, $\text{Al}_2(\text{SeO}_3)_3$ [2] and $\text{Ge}(\text{SeO}_3)_2$ have much lower cation radii ($r_{\text{Al}^{3+}} = 0.50 \text{ \AA}$ and $r_{\text{Ge}^{4+}} = 0.53 \text{ \AA}$), their thermal stability is lower and they start to decompose at significantly lower temperatures without melting.

Another important result was that the change of entropy for the formation of the active complex of the reagent ΔS^\ddagger decreased by absolute value from germanium to tin selenite remaining negative in all cases. The latter suggests that the formation of the active complex was accompanied by a decrease of entropy, i.e. the degree of structural arrangement of the active complex was higher than that of the initial selenite. The higher change of entropy was registered for $\text{Ge}(\text{SeO}_3)_2$ and smaller for $\text{Sn}(\text{SeO}_3)_2$ which means that the decomposition of the first selenite was connected with more substantial restructuring while the rearrangement of the sec-

ond one was less significant. This is an indirect confirmation for the stronger effect of counterpolarization of Ge^{4+} ion compared to Sn^{4+} ion.

The third fact which should be noted is the significantly lower than unity value of the steric factor P . It was indicated that the thermal decomposition of the selenites studied can be classified as ‘slow’ reaction [40,41]. The increase of P from $\text{Ge}(\text{SeO}_3)_2$ to $\text{Sn}(\text{SeO}_3)_2$, however, cannot compensate for the higher values of the activation energy. Therefore, the rate of the thermal decomposition decreased by the same order, from germanium to tin selenite. Obviously, the entropy component can not compensate the energy component for the rearrangement of the molecule.

It can be concluded that the thermal stability and, respectively, the rate of decomposition of the selenites from IVB group of the periodic system is directly connected with cation radii, their electron polarizability and the resulting different degrees of the effect selenite ion counterpolarization.

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