



## KINETICS AND MECHANISM OF THE THERMAL DECAY OF THE RADICALS FORMED DURING THE RADIOLYSIS OF SODIUM SELENATE

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Received October 5, 2009

Electron spin resonance spectra of free radicals formed in the radiolysis of polycrystalline sodium selenate  $\text{Na}_2\text{SeO}_4$  has been recorded. The accumulation with dose and the kinetics of the decay of the  $\text{Se}\dot{\text{O}}_4^-$ ,  $\text{Se}\dot{\text{O}}_3^-$  and  $\text{Se}\dot{\text{O}}_2^-$  radicals at higher temperature have been studied. A possible mechanism of thermal decay of these species is suggested.

### INTRODUCTION

Sodium selenate is an insecticide used to combat insects that attack non-edible plants; fertilization with sodium selenate increases selenium accumulation in soil.<sup>1</sup> The studies concerning the evaluation of the agents and procedures that have the potential to protect against acute and late effects of ionizing radiation damage of sodium selenate, as well.<sup>2</sup> Sodium selenate belongs to a large class of substances, such as  $\text{NaNH}_4\text{SeO}_4$ ,  $\text{K}_2\text{SeO}_4$  which present ferroelectric transition.

Gamma irradiation of  $\text{Na}_2\text{SeO}_4$  produces paramagnetic species identified as:  $\text{Se}\dot{\text{O}}_2^-$ ,  $\text{Se}\dot{\text{O}}_3^-$  and  $\text{Se}\dot{\text{O}}_4^-$  as it has been shown.<sup>3</sup> The radicals  $\text{Se}\dot{\text{O}}_2^-$  and  $\text{Se}\dot{\text{O}}_3^-$  are observable at room temperature. The radical  $\text{Se}\dot{\text{O}}_4^-$  is used as a probe of structural phase transitions in  $\text{Na}_2\text{SeO}_4$ .<sup>4-5</sup>

The present paper deals with information obtained by means of ESR spectra during the radiolysis of polycrystalline  $\text{Na}_2\text{SeO}_4$ , in order to characterize the spectral properties and the thermal behavior of radicals. The kinetics of the thermal

decay of radicals is important because of the indirect information obtained about the influence of different factors on the concentration of paramagnetic centers formed radiolitically.<sup>6</sup>

### EXPERIMENTAL

Anhydrous powdery  $\text{Na}_2\text{SeO}_4$  (BDH, p.a.) was used. Selenate samples were irradiated with gamma rays at room temperature, using a  $^{60}\text{Co}$  source of activity 500 Ci. The irradiation doses were of the order  $10^2$ - $10^5$  Gy.

The ESR spectra of the irradiated samples were recorded by means of a spectrograph ART 5. This spectrograph operates in the X band, with a high frequency modulation of 100 kHz. For the determination of the  $g$  factor the ion  $\text{Mn}^{2+}$  in a matrix of CaO was used as a standard.

### RESULTS AND DISCUSSION

Samples of anhydrous  $\text{Na}_2\text{SeO}_4$  irradiated with  $\gamma$  rays at room temperature become red colored and present intense similar ESR spectra. The value of the factor  $g$  measured at the point where the signal crosses the X-axis is  $\langle g \rangle = 2.01188$ . Such a spectrum is shown in Figure 1.

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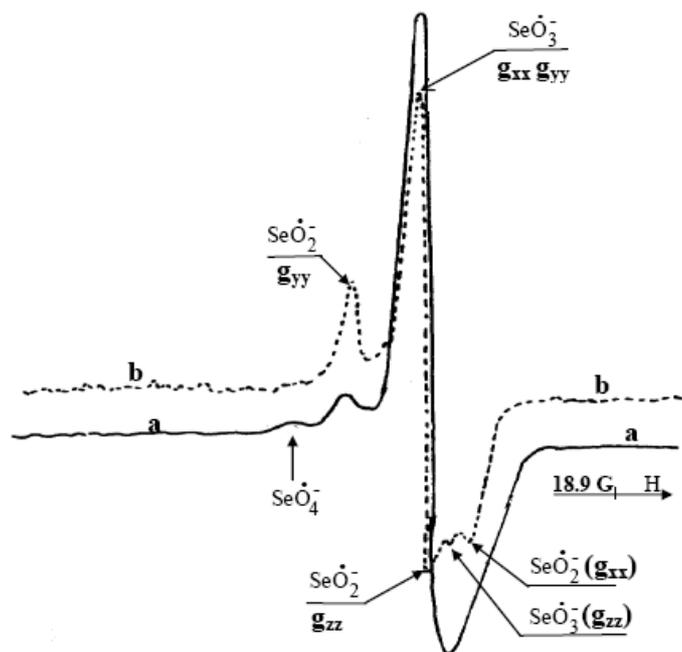


Fig. 1 – ESR spectrum of an irradiated sample of  $\text{Na}_2\text{SeO}_4$ :  
 (a) at room temperature; (b) the same sample after heating during 30 minutes at  $200^\circ\text{C}$ .

By irradiation of polycrystalline  $\text{Na}_2\text{SeO}_4$ , at room temperature (Figure 1), three radicals are formed in different proportions. The ESR spectrum recorded at room temperature represents a superposition of the spectra of three species:  $\text{SeO}_4^{\cdot-}$ ,  $\text{SeO}_3^{\cdot-}$ ,  $\text{SeO}_2^{\cdot-}$ , whose distinct components are indicated in Figure 1. The identification of the radicals was done in a previous paper<sup>6</sup> by comparing the value of the  $g$  factor, calculated from the spectra of irradiated samples of this selenate with those from literature determined for the same substance but of another provenance<sup>3,7</sup> or for other oxianions which generate via irradiation radicals with similar electronic structures.<sup>8-9</sup>

Generally, any radiolysis mechanism involves two processes: a primary one followed by a secondary one. The primary process is related to the species resulting from the direct action of radiations upon the reactant - in our case the anion  $\text{SeO}_4^{2-}$  and consists from the ionization ( $\text{SeO}_4^{2-} \xrightarrow{\gamma} \text{SeO}_4^{\cdot-} + e^-$ ) as well as from the excitation of the anion, when the energy received by it is not sufficient for ionization. The excited molecular ion ( $\text{SeO}_4^{2-}$ )\* being unstable decomposes with oxygen removal generating the radicals  $\text{SeO}_3^{\cdot-}$  and  $\text{SeO}_2^{\cdot-}$ .

The energy of the electrons ejected from anions by radiations can be comparable to that of the incident photons, which generated them. These

electrons loose energy by ionizing and exciting the anions  $\text{SeO}_4^{2-}$  with formation of radicalic entities similar to those generated by the incident radiation. The secondary electrons get finally to thermal energies, by loosing their kinetic energy through nonelastic collisions (thermalized electrons).

The thermalized electrons ( $e_{\text{term}}$ ) can be involved further in the following processes: to be trapped in the crystalline lattice, to be captured by  $\text{Na}^+$  cations or to recombine with radical species formed by radiolysis transforming them into non paramagnetic entities presented in Schemes 1 and 2 (1e, 1f, 2c, 2e).

The thermalized electron may be also trapped at an adjacent  $\text{SeO}_4^{2-}$  ion to form the  $\text{SeO}_4^{\cdot-}$  centre<sup>7,8</sup>.

The  $\text{SeO}_4^{\cdot-}$  center is unstable at the irradiation temperature; it gives rise to  $\text{SeO}_3^{\cdot-}$  and  $\text{SeO}_2^{\cdot-}$  paramagnetic species by decomposition. In the absence of impurities, the electron  $e_{\text{therm}}$  can return to the  $\text{SeO}_4^{\cdot-}$  radical resulting in the excited anion ( $\text{SeO}_4^{2-}$ )\*, which decomposes with generation of paramagnetic entities indicated in Figure 1. The intense central line from Figure 1 is assigned to the  $\text{SeO}_3^{\cdot-}$  radical previously detected at  $\text{K}_2\text{SeO}_4$  irradiation.<sup>3</sup> The  $g$  tensor of this radical has axial symmetry with the following values:  $g_{\pm}=2.0136$  and  $g_{\parallel}=2.0030$  ( $g_m=2.010$ ) attributed to the 4s and 4p orbitals of selenium. The considerable higher

value of  $g_{\pm}$  of  $\text{SeO}_3^-$  compared with that of  $\text{SeO}_3^-$  ( $g_{\pm}=2.0036$ ) is due to the higher value of the spin-orbit coupling constant of selenium.

The  $g$  tensor of  $\text{SeO}_2^-$ , calculated from the spectrum of the irradiated sample of  $\text{Na}_2\text{SeO}_4$  after heating at  $260^\circ\text{C}$  presents rhombic symmetry with

the values  $g_x=1.9989$ ,  $g_y=2.0279$ ,  $g_z=2.0095$ , ( $g_m=2.0121$ ).

The three radicals have different thermal stabilities. Indeed, after heating, the ESR spectrum structure of irradiated samples of  $\text{Na}_2\text{SeO}_4$ , changes. This behavior is shown in Figure 2, which contains the spectra of an irradiated sample, recorded at three temperatures.

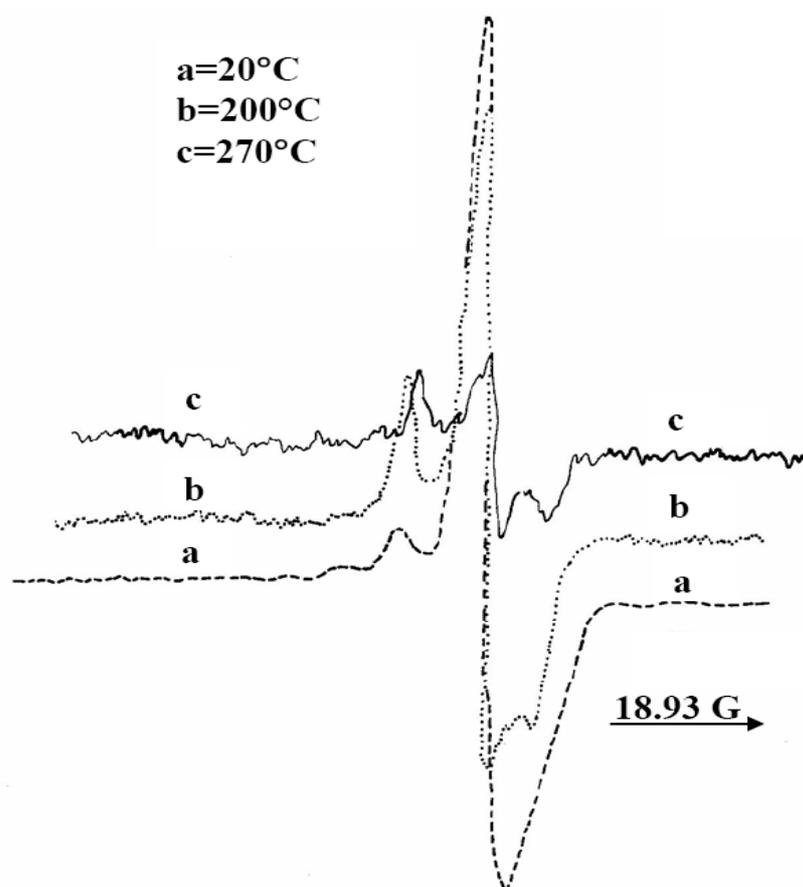


Fig. 2 – The irradiated sample of  $\text{Na}_2\text{SeO}_4$  spectra: a) initial ( $20^\circ\text{C}$ ), b) 10 minutes heated at  $200^\circ\text{C}$  c) 10 minutes heated at  $270^\circ\text{C}$ .

When heating the irradiated sample at temperatures exceeding  $260^\circ\text{C}$  the spectrum shape does no more change. The spectrum recorded after heating beyond  $260^\circ\text{C}$  is attributed to the  $\text{SeO}_2^-$  radical, which has the highest thermal stability.

Irradiation of samples with equal mass but for different times was carried out at room temperature, in order to follow the accumulation of the paramagnetic centers with the irradiation dose. Figure 3 shows the intensity of the central line (arbitrary units) of the spectra of samples of selenate, as a function of the time of irradiation (integral dose).

It may be noticed from Figure 3 that for low doses of irradiation, the concentration of radicals proportionally increases with the dose; the increase becomes slower starting from a dose of  $0.6 \cdot 10^4$  Gy. The curve reaches a maximum at  $2.6 \cdot 10^4$  Gy and then the radical concentration starts to decrease at higher doses. The decrease in radical concentration at higher doses is a proof that the radiolytic process involves not only the formation but also the decay of radicals under the action of gamma radiation. The predominant effect of gamma rays upon the sample of  $\text{Na}_2\text{SeO}_4$  becomes that of radicals destruction and not that of formation, which is the prevalent process at small doses.

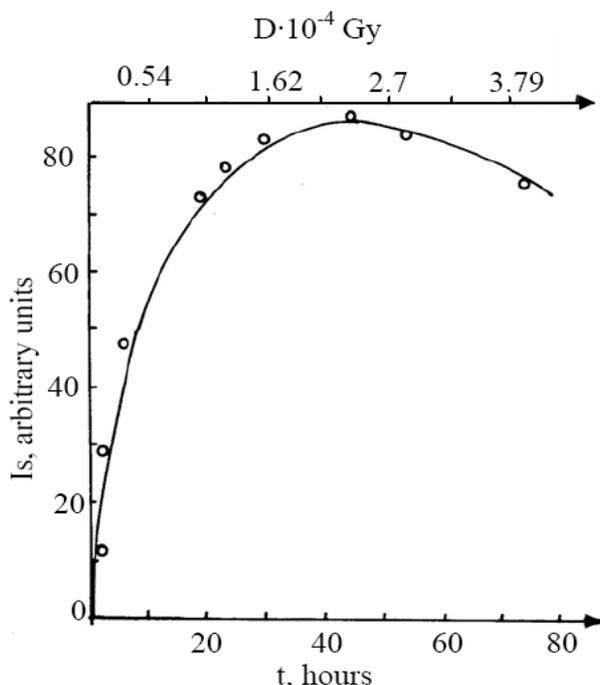


Fig. 3 – Variation of the intensity of the ESR signal of irradiated  $\text{Na}_2\text{SeO}_4$  with the integral dose.

The radical stability has been studied in function of temperature, in isochronous conditions. For this purpose, the irradiated sample of  $\text{Na}_2\text{SeO}_4$  was isothermally heated for 10 minutes at temperatures differing by  $10^\circ\text{C}$ , from room temperature up to the temperature at which the complete decay of the radicals was noticed ( $300^\circ\text{C}$ ).

The ESR signal was recorded after each heating step, in identical conditions. The data of signal amplitude measurements corresponding to the  $\text{Se}\dot{\text{O}}_4^-$ ,  $\text{Se}\dot{\text{O}}_3^-$ ,  $\text{Se}\dot{\text{O}}_2^-$  species, are analyzed below.

The component of the spectrum ascribable to the  $\text{Se}\dot{\text{O}}_4^-$  species is the only one which decreases on heating, starting from room temperature and disappears completely at  $115^\circ\text{C}$ . This proves that

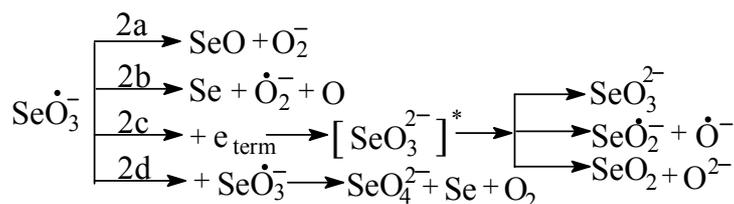
the  $\text{Se}\dot{\text{O}}_4^-$  radical has the lowest thermal stability. The thermal behavior of the above mentioned species found by us, agrees with information from literature,<sup>10-11</sup> referring to the same radical which is formed at the irradiation of all compounds containing the anion  $\text{SeO}_4^{2-}$ .

In Scheme 1 are shown the possible pathways that can be undertaken by the radical  $\text{Se}\dot{\text{O}}_4^-$  during the process of thermal decay.

It is seen in Scheme 1 that the  $\text{Se}\dot{\text{O}}_4^-$  radicals can decay by the following reactions: formation of stable species ( $\text{SeO}_4^{2-}$ ,  $\text{O}_2$ , selenium oxides, elemental selenium), formation of other radicals ( $\text{Se}\dot{\text{O}}_3^-$ ,  $\text{Se}\dot{\text{O}}_2^-$ ,  $\dot{\text{O}}_2^-$ ,  $\dot{\text{O}}^-$ ), radical-radical (1c) and radical-electron (1e, 1f) recombination.<sup>4,7</sup>

The weight of each possible pathway depends on several factors, essentially the same as those which influence the radiolysis process, such as the morphology of crystals, the type and density of lattice defects, the nature and concentration of impurities.

The plot from Figure 4 shows the variation of the intensity of the line ascribable to the ion-radical  $\text{Se}\dot{\text{O}}_2^-$  in function of the isochronous heating temperature up to  $300^\circ\text{C}$ .



Scheme 1 – Reaction involved in the thermal decay of the radical-anion  $\text{Se}\dot{\text{O}}_4^-$ .

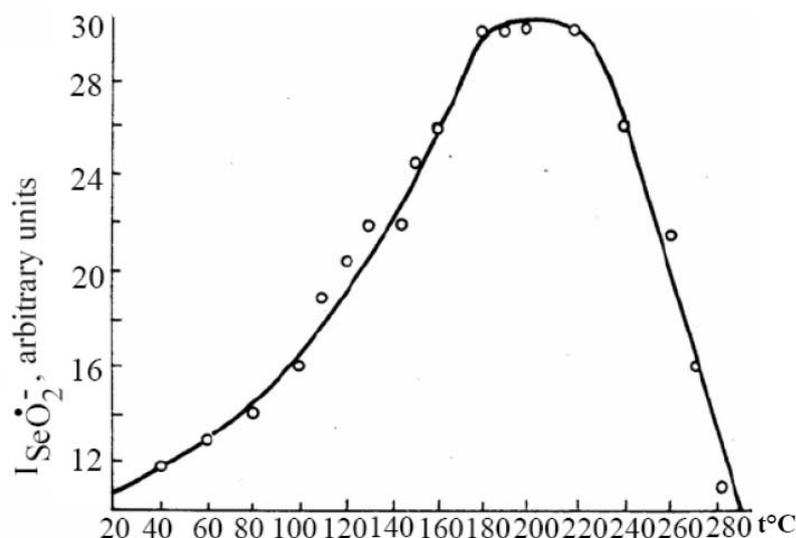


Fig. 4 – Dependence of the intensity of the  $\text{Se}\dot{\text{O}}_2$  signal on the isochronous heating temperature.

It is noticed from Figure 4 that the concentration of the radical  $\text{Se}\dot{\text{O}}_2$  increases from room temperature until  $190^\circ\text{C}$ , when a maximum is reached. This increase is due to  $\text{Se}\dot{\text{O}}_2$  formation because of  $\text{Se}\dot{\text{O}}_4^-$  and  $\text{Se}\dot{\text{O}}_3^-$  radicals decay (Schemes 1 and 2). Between  $190^\circ\text{C}$  and  $230^\circ\text{C}$ , the

concentration remains constant and decreases after that. The plot of  $\ln I_{\text{Se}\dot{\text{O}}_2}$  in function of temperature for the ascendant part of the curve from Figure 4 yields a straight line (Figure 5). The chart from Figure 5 shows an exponential growth of the signal of  $\text{Se}\dot{\text{O}}_2$  species up to  $180^\circ\text{C}$ .

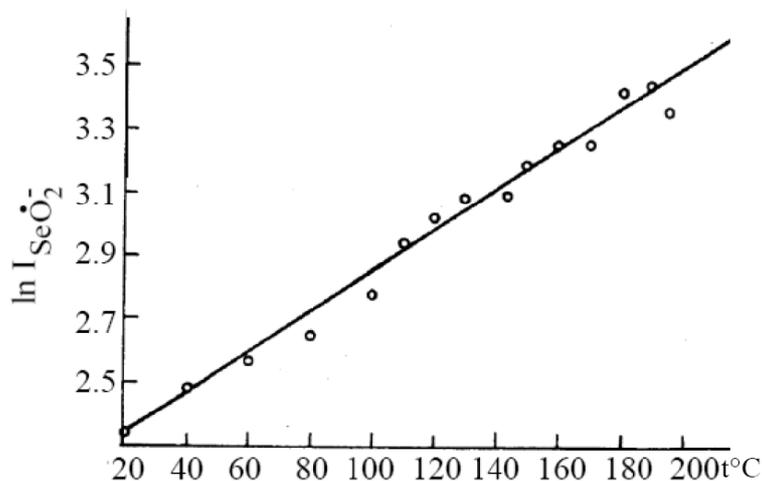


Fig. 5 – Variation of  $\ln I(\text{Se}\dot{\text{O}}_2)$  in function of temperature in the range  $20 - 200^\circ\text{C}$

A slight growth of the ESR spectrum component ascribable to the  $\text{Se}\dot{\text{O}}_3^-$  species was also observed up to  $80^\circ\text{C}$ . This proves the possibility of transformation of  $\text{Se}\dot{\text{O}}_4^-$  species into  $\text{Se}\dot{\text{O}}_3^-$ , too (Scheme 1).

The formation of these two radicalic entities ( $\text{Se}\dot{\text{O}}_3^-$ ,  $\text{Se}\dot{\text{O}}_2$ ) from  $\text{Se}\dot{\text{O}}_4^-$  is a result of different

mechanisms included in Scheme 1, depending on the bond between the atoms of the selenate ion-radical which is broken. According to Scheme 1, both reactions with oxygen removal accompanied by  $\text{Se}\dot{\text{O}}_3^-$  and  $\text{Se}\dot{\text{O}}_2$  radicals formation (1a, 1b, 1e) occur on heating, as well as recombination processes leading to  $\text{SeO}_4^{2-}$  parent ion reformation (1c).

The study of the kinetics of the thermal decay of  $\text{Se}\dot{\text{O}}_2^-$  radicals was performed by means of the reaction isotherms, i.e. the dependence of the

relative intensity ( $I/I_0$ ) of the radical  $\text{Se}\dot{\text{O}}_2^-$  signal versus time, at constant temperature (Figure 6).

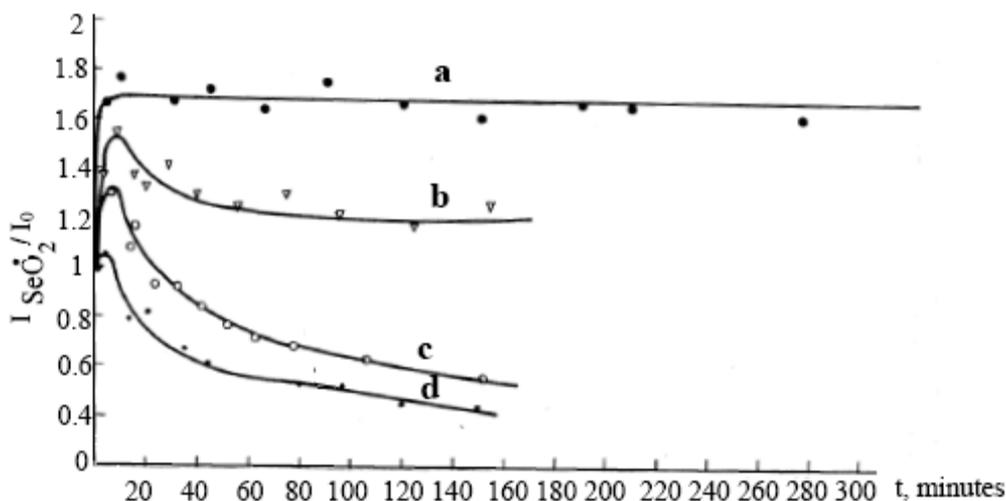


Fig. 6 – Isothermal variation of the signal amplitude of  $\text{Se}\dot{\text{O}}_2^-$  centres in function of the heating time: a) 190°C; b) 240°C; c) 260°C; d) 270°C.

The shape of each curve from Figure 6 confirms the behavior resulting from Figure 5. For instance, five minutes after the sample isothermal heating at 190°C (6a), the radical concentration increases by 70 %. If continuing the heating, its concentration remains constant. For the (6d) isotherm at a higher temperature (270°C), the concentration of the same species increases by only 5% after five minutes.

The behavior resulting from the isotherm analysis is explained by taking into account that if subjected to higher temperature the radicals  $\text{Se}\dot{\text{O}}_2^-$  are involved in two opposite processes: one of formation from  $\text{Se}\dot{\text{O}}_3^-$  and  $\text{Se}\dot{\text{O}}_4^-$  and the other of decay. The decay process prevails against that of formation as more as temperature is higher.

It is noticed from Figure 6 that all isothermal curves tend to a plateau at longer heating times. The lower is the heating temperature the higher is the plateau. The existence of a plateau in the above mentioned dependence proves that at any temperature strongly trapped radicals are present. These radicals are relatively stable because the thermal energy received from outside is lower than the necessary energy for their removal from the crystalline lattice. The vibration energy of the particles in the crystalline lattice increases with the temperature rise, a process which is accompanied by the weakening of the binding forces which maintain the trapped radicals.

The kinetics of the thermal decay of the  $\text{Se}\dot{\text{O}}_3^-$  radical species was investigated in a similar way, by plotting first the reaction isotherms (Figure 7).

With a view to this goal the radical concentration (proportional to the intensity of the ESR signal) was plotted versus the heating time.

The rates of the  $\text{Se}\dot{\text{O}}_3^-$  radical decay reactions at different temperatures was determined from the kinetic curves plotted in Figure 7. The ratio  $I/I_0$  was used in all the plots regarding the decay of  $\text{Se}\dot{\text{O}}_3^-$  radical in the range of temperature 190-270°C, in order that all isothermal curves start from the same point.

It is noticed in Figure 7 that at all temperatures the  $\text{Se}\dot{\text{O}}_3^-$  radical concentration decreases very fast only at the beginning of heating. After a short time ranging between 5 and 10 minutes a plateau is reached, corresponding to a lower concentration as the temperature is higher. The rate constants of this process could not be determined because it proceeds very fast.

The initial rates of the decay of  $\text{Se}\dot{\text{O}}_3^-$  radicals were calculated from the slope at the initial moment ( $v_{\text{in}} = -\frac{dc}{dt} = -\frac{d(I/I_0)}{dt} = \text{tg}\alpha$ ) where the reaction rate is maximum and the variation is practically linear (Figure 7). These values are listed in Table 1.

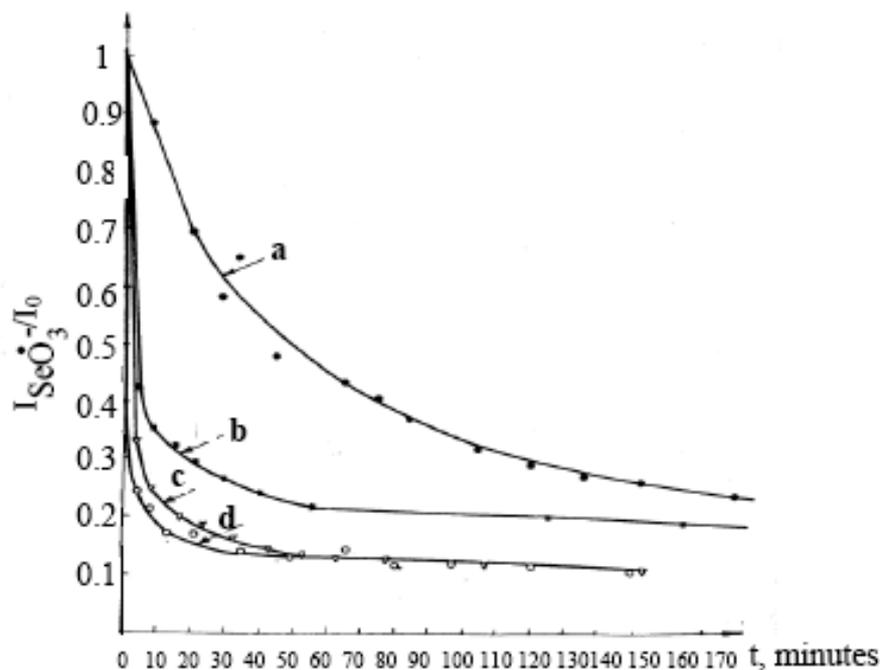


Fig. 7 – Isothermal variation of the  $\text{Se}\dot{\text{O}}_3^-$  signal amplitude in function of the heating time: a) 190°C; b) 240°C; c) 260°C; d) 270°C.

Table 1

The initial rate ( $v_{\text{in}}$ ) of the thermal decay of $\text{Se}\dot{\text{O}}_3^-$ and the rate constant for the $\text{Se}\dot{\text{O}}_2^-$ centers decay ( $k_3$ )					
$t^\circ\text{C}$	240	260	270	280	290
$v_{\text{in}} \cdot 10^{-3} (\text{s}^{-1})$	1.9	2.26	2.53		
$k_3 \cdot 10^{-6} (\text{s}^{-1})$		1.99	2.2	3.7	4.41

A kinetic study on the  $\text{Se}\dot{\text{O}}_2^-$  radicals decay was carried out after the total decay of the  $\text{Se}\dot{\text{O}}_3^-$  centers. The kinetic study of the  $\text{Se}\dot{\text{O}}_2^-$  radicals thermal decay has been performed within a temperature range (Figure 4) indicated on reaction isochronous. In order to study the radical recombination kinetics, the isothermal variation of ESR signal intensity versus time was analyzed at different temperatures. The working temperatures have been chosen in order to fulfill two conditions: first the reaction yield should be over 50 %, second the recombination process should not proceed very fast in order to reduce the experimental errors.

In order to establish the reaction order and calculate the rate constants different integer and fractional order (0, 0.5, 1, 1.5, 2, 2.5, 3) kinetic equations have been checked using the graphic method. We specify that the reaction order was established from the only graphical representation which gave a straight line. In this case we have obtained a straight line only for the plot corresponding to the third order equation (correlation coefficient 0.96). Because the radicals

concentration could not be determined, we have used the non dimensional parameter  $I/I_0$  ( $c \sim I$ ,  $c_0 \sim I_0$ ).

The rate constant was calculated from the slope of the straight line. We specify that the using of the ratio  $c^2=(I/I_0)^2$  does not modify the rate constant value because the straight lines are parallel and the calculated constants from the straight lines slope ( $\text{tg } \alpha=2k_3$ ) has the same value. The third order plot for the isotherm at 290°C is illustrated in Figure 8 while the rate constants  $k_3$  are listed in Table 1.

The activation energies of the  $\text{Se}\dot{\text{O}}_2^-$  and  $\text{Se}\dot{\text{O}}_3^-$  radicals decay processes were calculated with the Arrhenius equation  $k=Ae^{-E/RT}$  (or the similar equation for the reaction rate  $v = v_0e^{-E/RT}$ ) using the values of the constants and initial rates from Table 1.

The value of activation energy for  $\text{Se}\dot{\text{O}}_3^-$  ( $21.6 \pm 0.57 \text{ kJ mol}^{-1}$ ) is three times lower than that of  $\text{Se}\dot{\text{O}}_2^-$  ( $67.7 \pm 1.2 \text{ kJ mol}^{-1}$ ). This result is a quantitative confirmation that  $\text{Se}\dot{\text{O}}_2^-$  radicals have higher thermal stability than  $\text{Se}\dot{\text{O}}_3^-$  radicals, previously noticed.

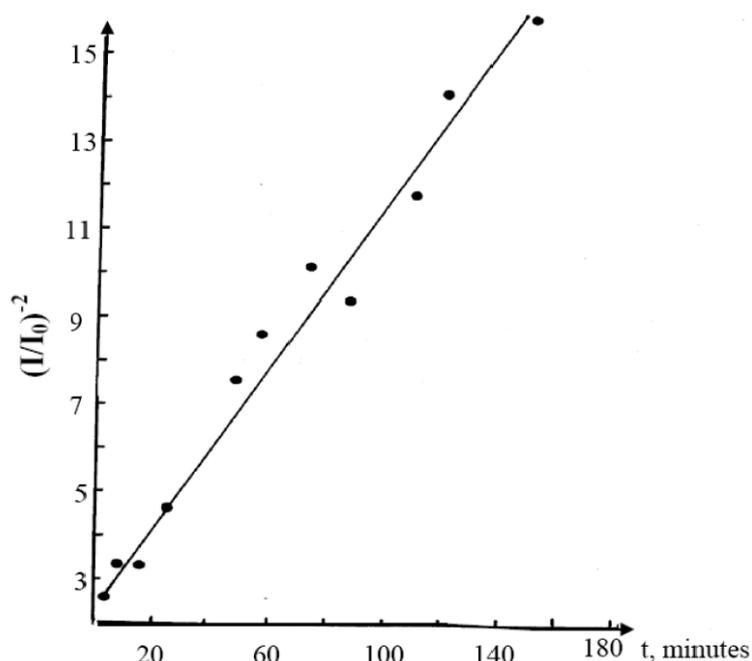
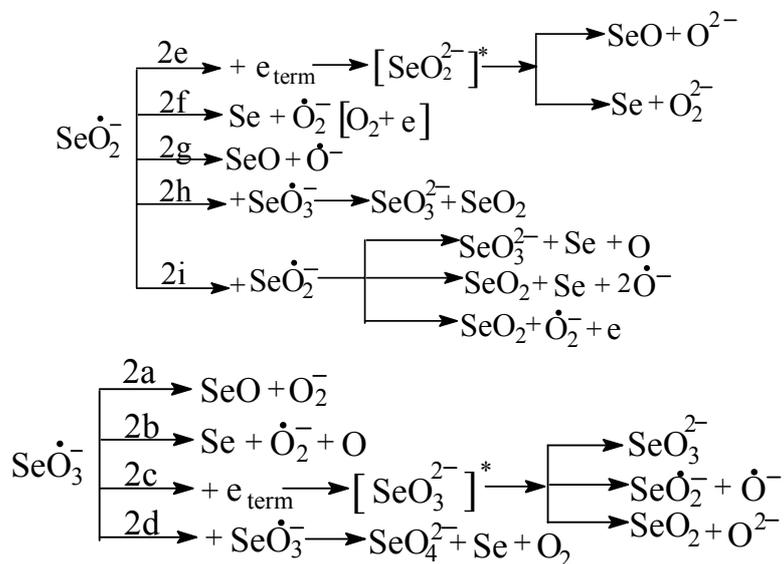


Fig. 8 –  $(I/I_0)^{-2}$  plot as a function of the heating time at 290°C.

The third order kinetics, found experimentally for the  $\text{Se}\dot{\text{O}}_2^-$  radicals decay, does not result from a trimolecular mechanism because this process would involve the simultaneous collision of three

radicals, impossible in the solid state. This order proves the existence of a complex decomposition and recombination process mechanism, involving several steps.



Scheme 2 – Chemical processes associated with the heating of the irradiated samples of  $\text{Na}_2\text{SeO}_4$ , involving  $\text{Se}\dot{\text{O}}_3^-$  and  $\text{Se}\dot{\text{O}}_2^-$  radicals decay.

The possible chemical processes produced at higher temperature in selenate irradiated samples<sup>7</sup> in which are involved  $\text{Se}\dot{\text{O}}_2^-$  and  $\text{Se}\dot{\text{O}}_3^-$  radicals, trapped in the crystalline lattice are shown in Scheme 2. Possible recombination reactions

between radicals of the same or different type (2d, 2h, 2i) resulting in nonparamagnetic species are included in Scheme 2, as well as reactions of the  $\text{Se}\dot{\text{O}}_2^-$  and  $\text{Se}\dot{\text{O}}_3^-$  radicals with secondary thermalized electrons, followed by molecular ions

formation in ground or excited state (2c, 2e). It also contains different radicals decomposition processes with elimination of atomic and molecular oxygen, in neutral, radicalic or ionic form (2a, 2b, 2f, 2g). A red colour of the irradiated heated samples, especially of those exposed to elevated temperature was noticed. This acknowledges the formation of elemental Se (1d, 2b, 2d, 2f, 2i), included between the reaction products from Schemes 1 and 2.<sup>7-8</sup> This finding is explained by the ease to be reduced to elemental selenium, of selenium dioxide and even more, of the monoxide.

Evidence for red Se formation during the heating of irradiated samples was obtained from diffuse reflectance spectra when a wide band in the region 240-270 nm was recorded, characteristic to elemental selenium.

### CONCLUSIONS

Three radical-anions:  $\text{Se}\dot{\text{O}}_4^-$ ,  $\text{Se}\dot{\text{O}}_3^-$ ,  $\text{Se}\dot{\text{O}}_2^-$ , identified by ESR are formed at the irradiation with gamma rays of polycrystalline  $\text{Na}_2\text{SeO}_4$  (BDH). An increase of the intensity of the lines of the radicals  $\text{Se}\dot{\text{O}}_3^-$  and  $\text{Se}\dot{\text{O}}_2^-$  from the ESR spectrum, simultaneously with the decay of the  $\text{Se}\dot{\text{O}}_4^-$  radical corresponding signal, proves that the later partially transforms into the two former above-mentioned radicals.

The thermal stability of the paramagnetic centers was investigated in the range between room temperature and 300°C. The thermal stability increases with the diminution of the number of oxygen atoms from the radical. This observation is consistent with information from

literature<sup>12-15</sup> regarding the radiolysis of inorganic salts. Several radical species are formed during the irradiation of an oxianion. The concentration and thermal stability is higher for the species corresponding to a lower oxidation state of the central element.

This study revealed that the  $\text{Se}\dot{\text{O}}_2^-$  species decay obeys a third order kinetics. A possible mechanism is proposed for the decay of the above-mentioned paramagnetic species.

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