KINETICS OF THE THERMAL DISAPPEARANCE OF RADICALS FORMED DURING THE RADIOLYSIS OF SODIUM TELLURATE (Na$_2$TeO$_4$ ·2H$_2$O)

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abstract: An EPR study of the paramagnetic centers formed by gamma irradiation of polycrystalline Na$_2$TeO$_4$ ·2H$_2$O (BDH) was made. In the EPR spectra recorded at room temperature, the presence of two types of radicals was observed; their thermal stability was investigated. The recombination kinetics of the radicals during thermal annealing has been studied. An adequate mechanism of radiolysis is proposed.

key words: sodium tellurate; paramagnetic centers; ionizing radiation; thermal disappearance.

1. Introduction

In the literature there are some information regarding the EPR studies of γ irradiated tellur oxycompounds. Constantinescu et al. [1] reported the formation of paramagnetic center formed at the irradiation of polycrystalline K$_2$TeO$_4$ and Na$_2$TeO$_4$. They have identified the following radicals: $\text{Te}\dot{\text{O}}_3^-$ and $\text{Te}\dot{\text{O}}_2^-$. Subsequently Baran et al. [2] and Rakitina et al. [3] have been studied the effects produced by irradiation in TeO$_2$ monocrystals, they found vacancies resulted from the oxygen removed. These vacancies may trap electrons generating radicals. The radiolysis with gamma radiation of telluric acid in solid polycrystalline state was performed at room temperature [4]. The EPR spectra recorded after radiolysis allowed the identification of three paramagnetic centers: $\text{Te}\dot{\text{O}}_4^-$, $\text{Te}\dot{\text{O}}_3^-$, $\text{Te}\dot{\text{O}}_2^-$.

In the present paper we studied by EPR the behaviour under irradiation at room temperature of polycrystalline Na$_2$TeO$_4$ ·2H$_2$O (BDH) examining the formation and disappearance of paramagnetic centers as well as their nature. The recombination kinetics of radical species is studied by EPR and their rate constants are determined.

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2. Experimental

The polycrystalline samples of $Na_2TeO_4 \cdot 2H_2O$ (BDH) have been irradiated with gamma rays at room temperature by using a ^{137}Cs source having $23.54 \cdot 10^{12}$ Bq activity and a dose rate of $1.05 \cdot 10^2$ Gy/h. The EPR spectra were recorded with an EPR spectrometer ART 5 operating in the X band having 100 kHz modulation. Mn^{2+} ion in CaO matrix was used as a standard for determining g factor.

3. Results and discussion

The EPR spectra for the γ irradiated of the polycrystalline $Na_2TeO_4 \cdot 2H_2O$ at room temperature are illustrated in Fig. 1.

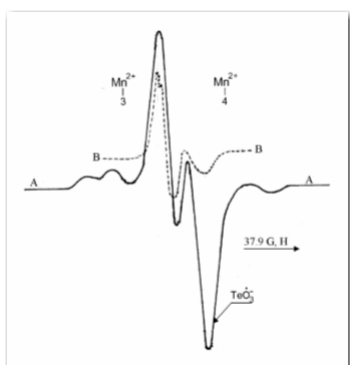Fig. 1 *EPR spectrum of the $Na_2TeO_4 \cdot 2H_2O$ irradiated with $10^4 Gy$:A) non heated sample, B) same sample heated 10 minutes at 160°C.*

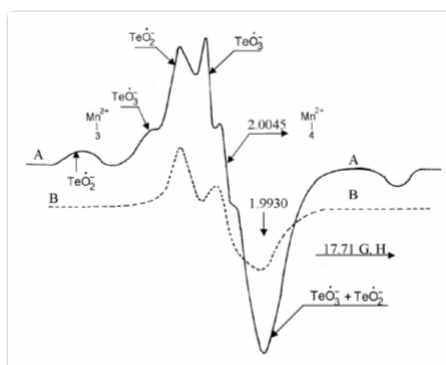Fig. 2 *EPR spectrum of the $Na_2TeO_4 \cdot 2H_2O$ gamma irradiated with $5 \cdot 10^5 Gy$:A) at room temperature, B) Same sample heated 5 minutes at 190°C.*

The spectra from Fig. 1 consists of two components. Examining the intensity variation of the two spectral lines with the temperature increasing, it can be noticed a different behaviour. The second component decreases more rapidly than the first (Fig. 1B). In Fig. 1B is shown the irradiated sample spectra after heating for 10 minutes at 160°C. The variation with temperature of the spectral lines intensities proves the existence of two radical species.

Tellurites of the alkali metals shows analogy with the corresponding selenates, therefore is useful to compare the radiolysis of these salts. By analogy with the radicals nature that form on similar Se compounds irradiation [5] results that the spectrum from Fig. 1A arises from the radicals $Te\dot{O}_3^-$ and $Te\dot{O}_2^-$ overlapping spectra [1].

The identification of these radicals formed by irradiation at room temperature is difficult because their spectra are similar and overlap having axial symmetry [6]. From literature it is known that in the case of selenates irradiation [7,8] the radicals thermal stability increases in the following order: $Se\dot{O}_4^-$, $Se\dot{O}_3^-$, $Se\dot{O}_2^-$ in the same time with the decrease of the oxidation state. The same behaviour it is also ascertained in the case of $Na_2TeO_4 \cdot 2H_2O$

which generates through irradiation the radicals $\text{Te}\dot{\text{O}}_4^-$, $\text{Te}\dot{\text{O}}_3^-$, $\text{Te}\dot{\text{O}}_2^-$, isoelectronic with selenium ones. Since radical $\text{Te}\dot{\text{O}}_4^-$ is only obtained by irradiation at 77 K [9] it must be a precursor of $\text{Te}\dot{\text{O}}_3^-$ and $\text{Te}\dot{\text{O}}_2^-$ formed at room temperature.

As $\text{Te}\dot{\text{O}}_2^-$ radical has higher thermal stability than $\text{Te}\dot{\text{O}}_3^-$ radical, results that the first component of the Fig. 1A doublet being more stable is mainly assigned to the $\text{Te}\dot{\text{O}}_2^-$ radical and the second one which disappear faster, to the $\text{Te}\dot{\text{O}}_3^-$ radical being the entity that are formed mainly with low doses.

By high doses (10^5-10^6) Gy irradiation at room temperature of Na$_2$TeO$_4$ ·2H$_2$O, spectrum structure modification is found (Fig. 2A). This behaviour is an additional proof of two radical species formation. The modification of the EPR spectrum structure from Fig. 2 by irradiation of Na$_2$TeO$_4$ ·2H$_2$O with high dose is due to the $\text{Te}\dot{\text{O}}_2^-$ radical formation having a higher concentration from $\text{Te}\dot{\text{O}}_3^-$ radical. Indeed, from Fig. 2B it can be seen that after irradiated sample heating to 190°C for 5 minutes, the disappearance of the two central lines belonging to $\text{Te}\dot{\text{O}}_3^-$ radical occurs. If the heating process is continued to 190°C the spectra shape is no longer changed, proving that belongs only to $\text{Te}\dot{\text{O}}_2^-$ radical. According our experiments, the g tensor is axially symmetryc for this radical g⊥=2.0132, g∥=2.0021.

In conclusion, the radiolitically formed $\text{Te}\dot{\text{O}}_3^-$ and $\text{Te}\dot{\text{O}}_2^-$ radicals concentration depends on irradiation dose.

The EPR spectrum from Fig 2A consist of a strong central line arising from the interaction of unpaired electron with nucleus [127]Te isotopes with nuclear spin I=0, having 93% natural abundance. The presence in the spectrum from Fig. 1A and Fig. 2A of two wide lateral components (ΔH=19.5 G) belong to the same radicals ($\text{Te}\dot{\text{O}}_3^-$ and $\text{Te}\dot{\text{O}}_2^-$) are due to the odd electron interaction of centers $\text{Te}\dot{\text{O}}_3^-$ and $\text{Te}\dot{\text{O}}_2^-$ with magnetic moment of [125]Te isotope having 7% natural abundance and nuclear spin I=1/2. The ratio of central line intensity and satellites intensity is approximately the same order with the natural abundance of the two tellurium isotopes with I=0 and I=1/2. The thermal stability of the radicals formed through radiolysis is a characteristic property of every kind of radical because it depends on both its chemical structure and crystalline network in which is formed through irradiation.

The thermal behaviour of paramagnetic $\text{Te}\dot{\text{O}}_3^-$ and $\text{Te}\dot{\text{O}}_2^-$ centers have been followed with isochronous reactions coordinate. In this purpose the sample has been gradually heated for 10 minutes for temperatures comprised within the room temperature and the temperature for which the complete vanishing of the radical is observed. The isochronous plotted in Fig. 3 may be interpreted as follows.
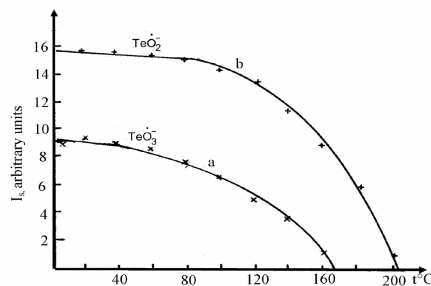
Fig. 3 *Isochronous variation of line intensity for* $Te\dot{O}_3^-$ *(a) and* $Te\dot{O}_2^-$ *(b) centers.*

It can be seen from Fig.3 that both $Te\dot{O}_3^-$ and $Te\dot{O}_2^-$ centers are stable until 70°C. From this temperature they gradually begin to disappear. The decay process characteristic curve of $Te\dot{O}_3^-$ radical start to decrease from 70°C and ends at 165°C. The $Te\dot{O}_2^-$ component intensity is stable untill 100°C then decrease gradually with temperature increasing and disappears completely at 220°C. After the complete disappearance of the $Te\dot{O}_3^-$ species at 170°C is recorded a single signal assigned to $Te\dot{O}_2^-$ radical. A similar behaviour was noticed in the case of selenates irradiation [10,11] indicating that the difference was the temperature range of decay process.

Plotting the reaction isochronous is a proof that the thermal stability of $Te\dot{O}_2^-$ radicals formed on $Na_2TeO_4 \cdot 2H_2O$ irradiation is higher than $Te\dot{O}_3^-$ radicals. It is also noticed that the range on both radicals decay takes place is wide.

Data on kinetics of paramagnetic centers were obtained by isothermal annealing of irradiated $Na_2TeO_4 \cdot 2H_2O$ samples within the temperature range indicated on the reaction isochronous. In order to study radical recombination kinetics the isothermal variation of EPR signal intensity against heating time at different temperatures was performed. The working temperatures have been chosen in order to fulfill two conditions: first the reaction yield be over 50%, second the recombination process takes place not so fast in order to reduce the experimental errors.

In Fig. 4 are plotted two isotherms corresponding to $Te\dot{O}_3^-$ and $Te\dot{O}_2^-$ species at 130°C. The reaction isotherms were plotted representing relative intensity (I_s/I_0) versus heating time. I_s is the intensity at t moment and I_0 represents the initial intensity.
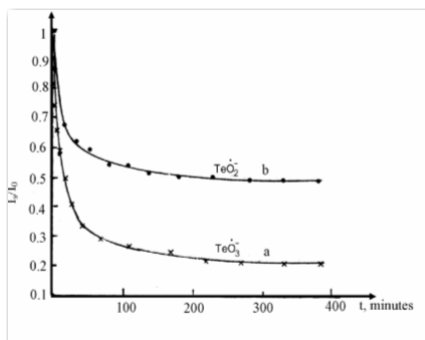
Fig. 4 *Isothermal variation of the intensity of the EPR signal at the 130°C for (a)* Te$\dot{\text{O}}_3^-$ *and (b)* Te$\dot{\text{O}}_2^-$ *centers.*
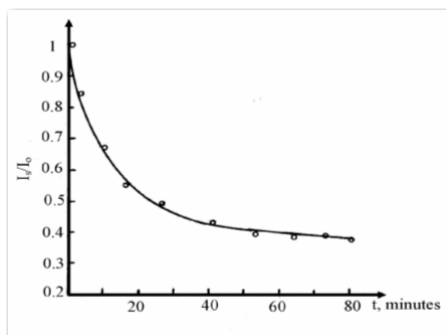
Fig. 5 *Variation of EPR line intensities for* Te$\dot{\text{O}}_2^-$ *function of heating time at 190°C*

From Fig. 4 it is found that at 130°C the component attributed to Te$\dot{\text{O}}_3^-$ radical shows first a greater decay rate from Te$\dot{\text{O}}_2^-$ radical. In Fig. 5 is plotted the isotherm recorded at 190°C belonging only to Te$\dot{\text{O}}_2^-$ species.

The paramagnetic centers trapped by crystalline network possess different binding energies depending on their sites and on the neighbour with they interact. We have mentioned that all isotherms are characterized by a plateau for longer heating time. The isothermal curves tend to a plateau located below the more as the temperature is higher. The appearance of a plateau proves the existence of radicals at each temperature, being more strongly trapped. These radicals are relatively stable because the thermal energy received from outside is lower than the necessary energy of their removal from the crystalline network. By temperature increase, the vibration energy of particles in crystalline network will be increased accompanied by the weakening of binding forces which maintain the trapped radicals. The isothermal variation of the two components relative intensity confirms the existence of the two radicals in Na$_2$TeO$_4$ ·2H$_2$O irradiated sample.

From Fig. 4 is ascertained that at 130°C while the Te$\dot{\text{O}}_2^-$ radical intensity reaches a plateau at 50 % from initial value, the Te$\dot{\text{O}}_3^-$ radical reaches the plateau after a 80% decay because it has a lower thermal stability.

In order to determine the reaction order and calculate the rate constants, the integral kinetic equations for all fractional and integers orders were plotted using the graphic method. The reaction order was established from the graphical representation which gave a straight line, the other representations were curves.

To calculate the reaction rates and rate constants it was used the dimensionless parameter (I_s/I_0) relative intensity instead concentration, where I_s is the signal intensity after each heating time and I_0 initial intensity.

For temperatures between 117-160°C plotting the reverse of the signal intensity $(I_s/I_0)^{-1}$ as a function of isothermal heating time, a straight line was obtained provided that the thermal

recombination process of $Te\dot{O}_3^-$ radicals verifies a second order kinetics. In Fig. 6 is shown this plotting for 117°C. From the slope of the plotted straight lines for different temperatures, the rate constants have been calculated.
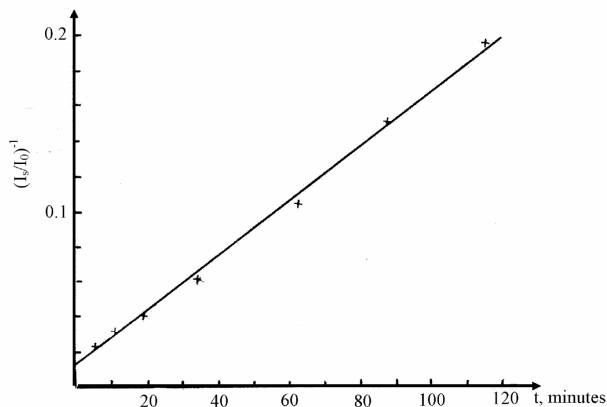

Fig. 6 *Variation of $(I_s/I_0)^{-1}$ ratio as a function of heating time at 117°C.*

From the values of the rate constants summarized in Table 1, it can be noted that there is not a significant growth with increasing temperature. Using Arrhenius type formula the activation energy has been found as being equal to 24.83±0.27 kJ/mol.

Table 1 *Kinetic parameters of the thermal annealing of $Te\dot{O}_3^-$ and $Te\dot{O}_2^-$ radicals.*

Radical	t,°C	T, K	$1/T$, K^{-1} 10^3	$k \cdot 10^5$, s^{-1}	lgk+5
Kinetics of 2nd order $Te\dot{O}_3^-$	117	390	2.5641	2.4805	0.3945
	130	403	2.4814	2.8943	0.4615
	150	423	2.3640	4.7666	0.6782
Kinetics of 1.5 order $Te\dot{O}_2^-$	170	443	2.257	1.666	0.2216
	180	453	2.207	4.359	0.6393
	190	463	2.159	7.101	0.8513

The value of this process activation energy has not the known significance from gaseous state kinetic theory where molecules move freely. In this case the $Te\dot{O}_3^-$ centers are trapped in the crystalline network and the recombination process takes place from increasing these species mobilities produced by temperature, the removal of the radicals from the occupied positions occurs when the vibration energy overcome the binding forces which maintain the radicals trapped.

Increasing the temperature, the network constituents vibration energy increases being accompanied by the weakening of the binding forces which maintain the trapped radicals.

For $Te\dot{O}_2^-$ radical the plot $(I_s/I_0)^{-1/2}$ versus the heating time under isothermal heating, it was obtained straight lines proving that the disappearance of this radical obeys the kinetics of fractional order 1.5. The plot $(I_s/I_0)^{-1/2}$ as a function of heating time at 170°C is shown for exemplification in Fig. 7.
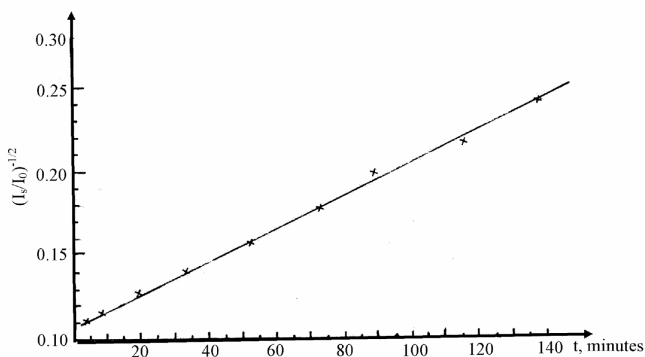

Fig. 7 *Variation of $(I_s/I_0)^{-1/2}$ versus heating time at 170°C.*

The values of the rate constants for each heating temperature were calculated from the slope of the straight lines (Table 1).

The kinetic study of $Te\dot{O}_2^-$ radicals decay was carried out after the total decay of the $Te\dot{O}_3^-$ centers. From the plotting lg$k$ versus $1/T$ the activation energy has been estimated as 122.44 ± 1.15 kJ/mol. The spectral and kinetic data experimental obtained enabled us to purpose a mechanism of radiochemical formation and thermal disappearance.

The primary process consists both in ionization and excitation of TeO_4^{2-} anion leading at radical generation ($Te\dot{O}_4^-$, $Te\dot{O}_3^-$, $Te\dot{O}_2^-$) and also to the expulsion of oxygen and electron. The $Te\dot{O}_4^-$ radicals are unstable at room temperature and convert into $Te\dot{O}_3^-$ and $Te\dot{O}_2^-$ by lose of oxygen atoms.
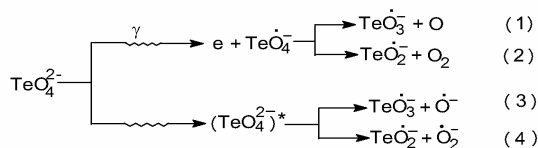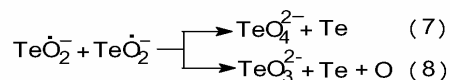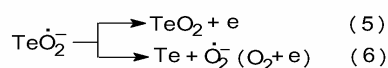

The energetic electrons removed from oxyanion, loose the kinetic energy by inelastic collisions, transferring this energy to the constituent atoms of the lattice. Finally these electrons become thermalized. In this state there are three possibilities:
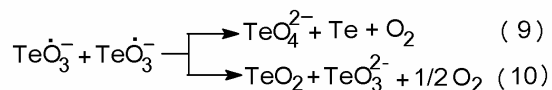
1. The electrons are trapped by the lattice defects even at the room temperature. By heating of the sample, the traps are depopulated and electrons recombine with $Te\dot{O}_4^-$ radicals leading to initial anion $(TeO_4^{2})^*$ in excited state. The last species decomposes giving paramagnetic entities.

2. The thermalized electrons attach to the initial ions forming paramagnetic centers of $Te\dot{O}_4^{3-}$ type. The existence of such species is reported in literature at radiolysis of Se [5,7] and Cr [12,13] oxyanions at 77 K. In the present case $Te\dot{O}_4^{3-}$, unstable at room temperature, decomposes by expulsion of an oxygen atom, forming the same $Te\dot{O}_3^-$ and $Te\dot{O}_2^-$.

3. The third possibility is the capture of the electrons by cations or different impurities existent in the sample during the synthesis of the process. As has been shown, the oxyradical $Te\dot{O}_2^-$ disappears according to a 1.5 order process. This supposes simultaneous existence of two processes namely of first and second order.

$$Te\dot{O}_2^- \begin{cases} \longrightarrow TeO_2 + e & (5) \\ \longrightarrow Te + \dot{O}_2^- \ (O_2 + e) & (6) \end{cases}$$

$$Te\dot{O}_2^- + Te\dot{O}_2^- \begin{cases} \longrightarrow TeO_4^{2-} + Te & (7) \\ \longrightarrow TeO_3^{2-} + Te + O & (8) \end{cases}$$

The thermal disappearance of radical $Te\dot{O}_3^-$ has shown a second order kinetic process. This behaviour corresponds to a process of this form:

$$Te\dot{O}_3^- + Te\dot{O}_3^- \begin{cases} \longrightarrow TeO_4^{2-} + Te + O_2 & (9) \\ \longrightarrow TeO_2 + TeO_3^{2-} + 1/2\,O_2 & (10) \end{cases}$$

A grey colour of the irradiated samples due to the metallic tellurium was noticed. Supplementary evidence for grey Te generation was obtained by recording the diffuse reflectance spectrum which exhibits a very broad band in the 230-580 nm region with no precise maximum positioning. It is formed by successive loose of oxygen from the radical parent anion under the action of irradiation. The O_2 molecules by heating of irradiated samples have been chromatographically proved.

Since the substance contains two water of crystallization molecules, in the radiolysis mechanism it must be also included the participation of resulted water radiolysis H and OH radicals. H atom being a reduction species can extract oxygen from the radical species existing in the system:

$$Te\dot{O}_3^- \xrightarrow[-OH]{+H} Te\dot{O}_2^- \xrightarrow[-OH]{+H} TeO \xrightarrow[OH]{+H} Te \qquad (11)$$
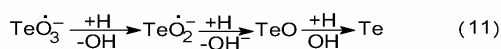
The production of these reactions justify the radicals $Te\dot{O}_3^-$ and $Te\dot{O}_2^-$ concentration changing with irradiation dose of the spectra structure shown in Fig. 1A and Fig. 2A.

4. Conclusions

The EPR spectra of the polycrystalline samples Na$_2$TeO$_4$ ·2H$_2$O (BDH) gamma irradiated at room temperature are the results of the superposition of two radicalic entities, presented in radiolysis mechanism. It was observed by studying the kinetic of thermal disappearance of the radical $Te\dot{O}_2^-$ that fits a fractionary kinetics (1.5) while the disappearance of the radical $Te\dot{O}_3^-$ follows a second order kinetics. The activation energies in the recombination process of $Te\dot{O}_3^-$ and $Te\dot{O}_2^-$ were calculated. A thermal recombination mechanism is proposed for these species corresponding to the experimentally verified kinetics.

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