



## THERMAL ANNEALING KINETICS OF RADICALS FORMED BY THE RADIOLYSIS IN POLYCRYSTALLINE SOLID STATE OF SODIUM WOLFRAMATE

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A kinetic study concerning  $WO_4$  radical produced by gamma irradiation at room temperature of polycrystalline  $Na_2WO_4 \cdot 2H_2O$  was performed using the EPR technique. A suitable mechanism of formation by irradiation and thermal annealing of paramagnetic centres is proposed. It agrees fairly well with experimental data.

### INTRODUCTION

In the literature there are only some papers concerning the tungsten oxygenated compounds<sup>1-2</sup>, which are based especially on the radicals identifying and determination from experimental data of EPR spectra parameters.

There is no information about  $Na_2WO_4 \cdot 2H_2O$  radiolysis and in addition is made the specification that this compound does not form radical species by irradiation<sup>3</sup>.

Paramagnetic centres formed by  $CaWO_4$  irradiation were established by Zelder and Livingston<sup>4</sup>. They reported the formation of  $WO_4^{\bullet-}$  radical in the radiolysis primary process. This radical in contrast with  $CrO_4^{\bullet-}$ <sup>5-6</sup> cannot exist per se and it stabilizes in the  $WO_4^{2-} - WO_4^{\bullet-}$  form, in which unpaired electron belongs to both wolfram nuclei. A corresponding process takes place also, in  $CaMoO_4$  irradiation<sup>7</sup>.

In a previous study<sup>8</sup> many factors influence on EPR spectra structure of  $Na_2WO_4 \cdot 2H_2O$  irradiated samples was put into evidence. These factors are: tungstate preparation method, lattice concrete structure and generally, macro and micro defects.

There is no information concerning the thermal behavior of paramagnetic centres formed by  $Na_2WO_4 \cdot 2H_2O$  irradiation, at room temperature.

In this study was performed the thermal disappearance kinetics of  $WO_4^{\bullet-}$  radicals and finally, was established the mechanism of this radiolytic process.

### EXPERIMENTAL

For irradiation were used polycrystalline samples of  $Na_2WO_4 \cdot 2H_2O$  Merck. The irradiations were performed at room temperature by  $\gamma$  rays from a <sup>137</sup>Cs source with 800 Ci activity and 1.05 Gy h<sup>-1</sup> dose rate.

EPR spectra of irradiated samples were recorded with an ART 5 spectrograph (IFIN Magurele), operating in the X band

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with a 100 kHz high frequency modulation. In order to determine the g factor was used  $Mn^{2+}$  ion in  $CaO$  matrix, as a standard.

## RESULTS AND DISCUSSION

By  $\gamma$  irradiation at room temperature of  $Na_2WO_4 \cdot 2H_2O$  Merck, in polycrystalline solid state, complex spectra are recorded (Figure 1).

The signal from Figure 1 belongs to radical with electron deficient,  $WO_4^{\cdot-}$ , with W in VII valence state, similar to  $CrO_4^{\cdot-}$ , obtained by

$CrO_4^{2-}$  irradiation<sup>5</sup>. The stability with temperature of  $WO_4^{\cdot-}$  ion-radical is higher than  $CrO_4^{\cdot-}$ , because divides its charge to unpaired electron with a  $WO_4^{2-}$  neighbor ion, in order to create a centre with two W atoms in the  $(W_2O_8)^{3-}$  form<sup>4</sup>, similar to  $Cl_2^{\cdot-}$  formation, by alkaline chloride irradiation<sup>9</sup>.

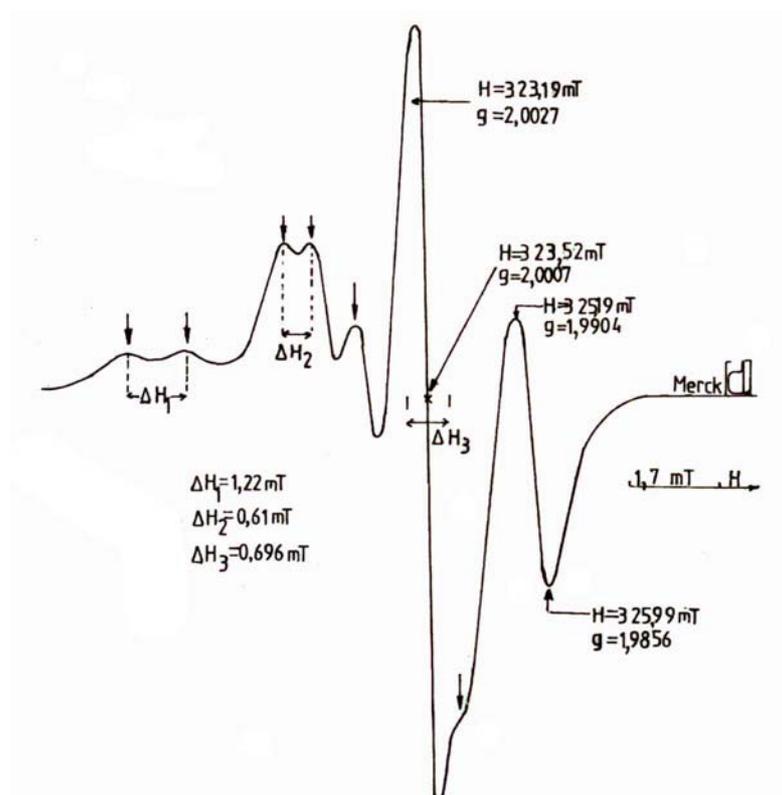


Fig. 1 – EPR spectrum of a  $Na_2WO_4 \cdot 2H_2O$  polycrystalline sample,  $\gamma$  irradiated at room temperature with a dose of  $2 \cdot 10^4$  Gy.

The expelled electron from the radiolysis primary process is captured by another ion  $WO_4^{2-}$  to form  $WO_4^{\cdot-}$  radical, with W in V valence state, stable at 77K, but unstable at room temperature<sup>8</sup>.

From Figure 1 we can observe that the spectrum is a complex one, because it has many components.

The hyperfine splitting existence in the EPR spectra of  $\gamma$  irradiated  $Na_2WO_4 \cdot 2H_2O$  has the following explanation: nuclei of W<sup>180, 182, 184, 186</sup> with 85,6 % natural abundance have the nuclear

spin equal with zero ( $I=0$ ) and <sup>183</sup>W isotope with 14,4% rest of natural abundance has an unpaired nuclear spin ( $I=1/2$ ).

Because the unpaired electron interacts with two nuclei of W, three types of  $(W_2O_8)^{3-}$  radicals are formed.

The central singlet with high intensity comes of the even isotopes species with two nuclei  $I=0$ , which represent 85,6%. Two spectra with hyperfine structure which proceed from unpaired

isotopes of W ( $I=1/2$ ), with 14,6% natural abundance, are recorded over central singlet as follows: a spectrum in the triplet or quartet form of the species with two unpaired nuclei  $I=1/2$  and a doublet comes from the species with two unequal nuclei ( $I=0, I=1/2$ ). Due to the superposition of the three radical entities is produced the hyperfine structure alteration because the three types of radicals formation proportion depend on concrete crystalline structure.

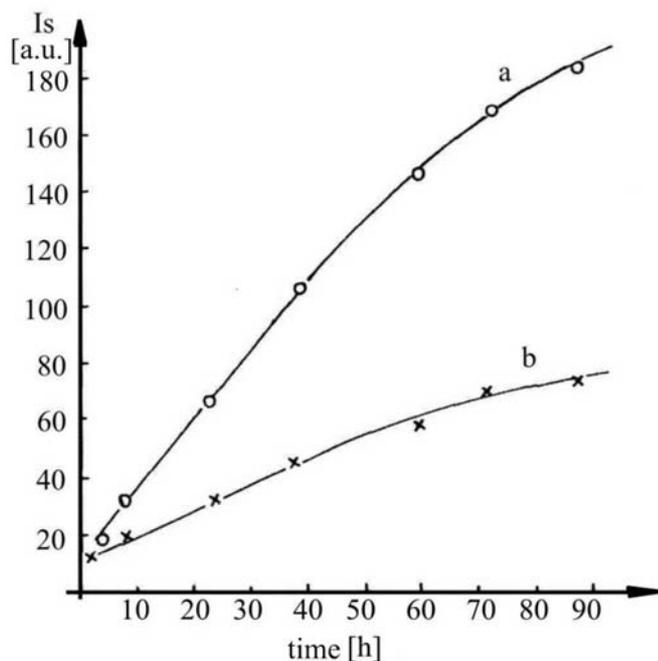


Fig. 2 – Variation of EPR signal intensity versus irradiation time (dose rate  $1.05 \cdot 10^2 \text{ Gy h}^{-1}$ ) a) Central singlet; b) Line from the right side of singlet.

For low doses the curves presents a linear increase and for high doses (over  $4 \cdot 10^3 \text{ Gy}$ ), occurs a gradually decrease. This behavior indicates the fact that for high doses (over  $4 \cdot 10^3 \text{ Gy}$ ), two competitive processes occur during irradiation: radicals formation and their disappearance.

The paramagnetic centres stability with temperature has been studied by means of reaction isochronous procedure. To this purpose, a  $\gamma$  irradiated sample was gradually heated for 5 minutes in stepwise (each step =  $10^\circ\text{C}$ ), from room temperature up to the temperature of the complete EPR signal disappearance. Thus, the irradiated sample has been maintained for the same period at each temperature.

As may be seen from Figure 3, the EPR signal intensity of  $W_2O_8$  linearly decreases starting from the room temperature up to  $60^\circ\text{C}$ .

In order to establish the accumulation of  $(W_2O_8)^{3-}$  paramagnetic centres with integral dose, equal weights of  $Na_2WO_4 \cdot 2H_2O$  samples were irradiated at different times. In Figure 2 is presented the variation curve of EPR signal intensity with irradiation time ( $1.05 \cdot 10^2$ , dose rate).

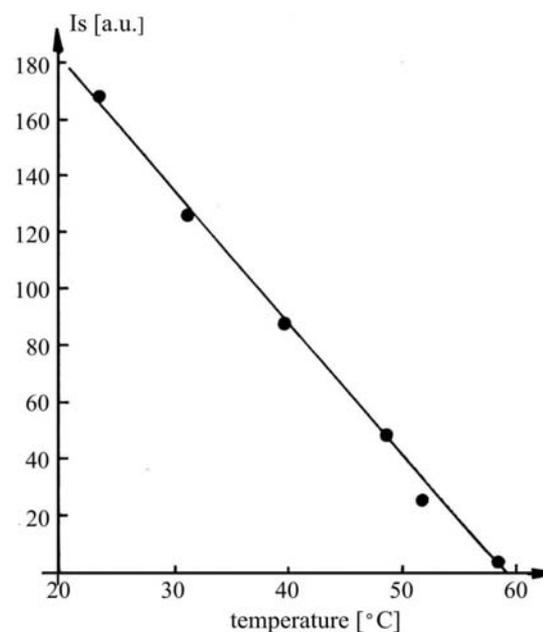


Fig. 3 – Isochronous variation of EPR signal intensity versus heating temperature of a  $\gamma$  irradiated  $Na_2WO_4 \cdot 2H_2O$  sample.

It is important to mention that after the sample heating at  $60^\circ\text{C}$ , remains a low intensity signal, more thermally stable comparatively with  $WO_4^{\bullet-}$ , attributed to  $WO_3^{\bullet-}$  radical, similarly to  $CrO_3^{\bullet-}$ .<sup>10-11</sup>

The kinetics of radicals thermal recombination was performed within the temperature range indicated on the reaction isochronous. The working temperatures have been chosen in order to fulfill two conditions: first, the reaction to occur in proportion to over 50% and second, the disappearance processes to occur not so fast in order to reduce the experimental errors.

In Figures 4a and 4b is plotted the variation of EPR signal relative intensity ( $I_r = I_s/I_0$ , where  $I_0$  represents initial intensity and  $I_s$ , the intensity at the “ $t$ ” time of isothermal heating) with the time of isothermal heating.

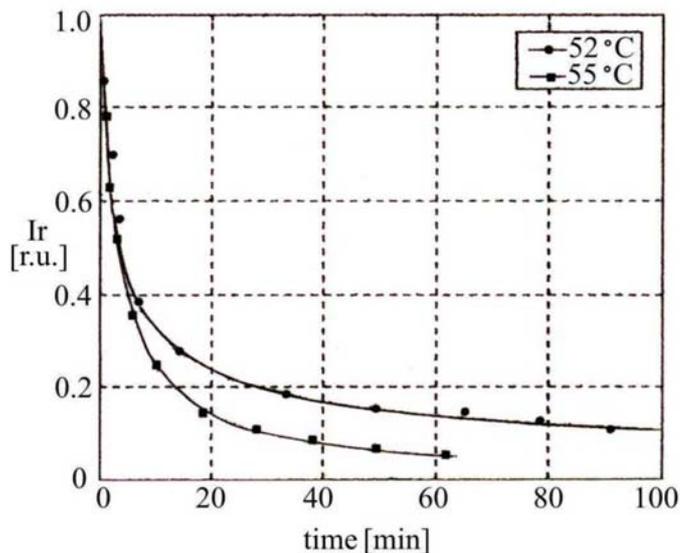


Fig. 4a

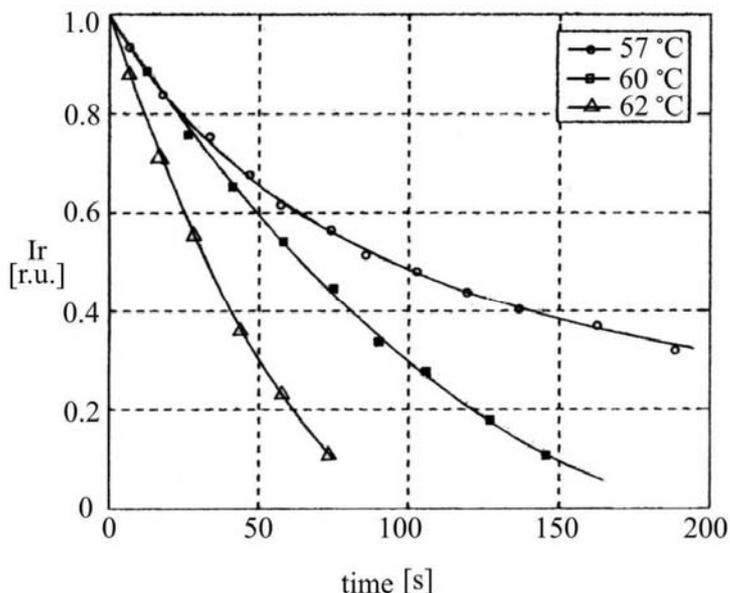


Fig. 4b

Fig. 4 – Variation of EPR signal intensity of  $\gamma$  irradiated and isothermal heated samples at the following temperatures: a) 52-55°C b) 57-62°C.

As may be seen from Figure 4, at the beginning of the heating process, the decreasing of radicals concentration is even faster as the temperature is higher. All the curves tend to a plateau situated the lower the higher is temperature. The plateau appearance proves the fact that radicals have different thermal resistance, because for each temperature remain the trapped radicals in crystalline lattice. For these radicals the energy received from exterior is lower than the binding energy.

The thermal annealing kinetics of radicals formed by  $Na_2WO_4 \cdot 2H_2O$  samples  $\gamma$  irradiation was performed within 52-62°C temperature range. For determination of reaction order and rate constants, the both kinetic methods: integral and differential were used.

In the integral method the established equations from chemical kinetics were verified, for all whole and fractionary reaction orders, with specification that radical concentration was changed with relative intensity of EPR signal ( $I_r$ ).

The plot diagram of each kinetic equation was made in linearized form, corresponding to all reaction orders. The straight lines were plotted that each slope to have the least error related to experimental points.

The experimental points are the best plotted on a line for the plotting of 2 order kinetic equation at 55°C temperature.

The rate constants have been calculated from 0 to 3 for thermal annealing of radicals at 55°C, by method of least squares (Table1), using the plot diagrams corresponding to the all reaction orders.

For verifying of the reaction order 2 obtained from isotherms plotted for each reaction order, the  $\Delta I_r$  deviation of each experimental point related to the adequate point on the regression line was

determined. The obtained values were related at the last point value on the regression line and like this, errors in percents ( $\varepsilon_{\max}$ ) have been calculated.

In Figure 6 is plotted the maximum relative error ( $\varepsilon_{\max}$ ) versus reaction order for 55°C isotherm.

It can be noticed that the maximum relative error linear decreases with increase of reaction order, reaches a minimum value at order 2 and after that increases linear, too. The same behavior was observed at all isotherms of reaction order establishing, using this method.

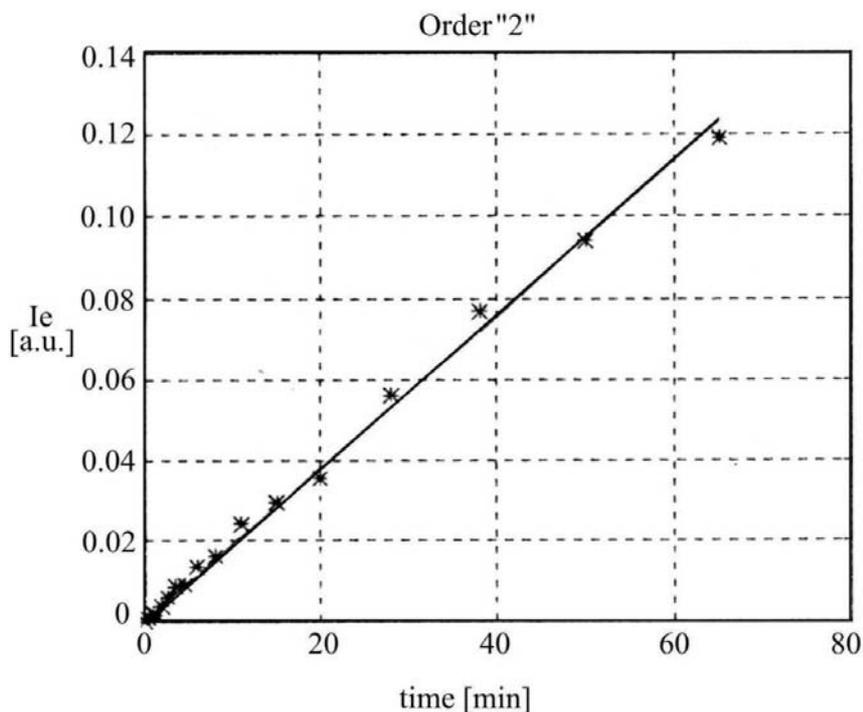


Fig. 5 – Plotting of kinetic equation corresponding to 2 reaction order versus time of isothermal heating at 55°C for a  $\gamma$  irradiated  $Na_2WO_4 \cdot 2H_2O$  sample.

Table 1

| Kinetic parameters and maximal relative errors determined for radical species disappearance at 55°C |                    |  |                     |                          |
|---|--------------------|--|---------------------|--------------------------|
| Crt. No.  | Reaction order "n" | k [s <sup>-1</sup> ] x 10 <sup>3</sup> | $\Delta I_r$ [a.u.] | $\varepsilon_{\max}$ [%] |
| 1   | 0                  | 0,381                                  | 0,55                | 37,17                    |
| 2   | 0,5                | 0,589                                  | 0,71                | 31,09                    |
| 3   | 1                  | 1,03                                   | 0,91                | 22,65                    |
| 4   | 1,5                | 2,12                                   | 1,03                | 12,45                    |
| 5   | 2                  | 5,12                                   | 0,083               | 4,16                     |
| 6   | 2,5                | 14,14                                  | 4,92                | 8,92                     |
| 7   | 3                  | 43,37                                  | 35,38               | 20,92                    |
| 8   | 3,5                | 143,33                                 | 178,69              | 31,96                    |
| 9   | 4                  | 499,83                                 | 818,26              | 41,98                    |

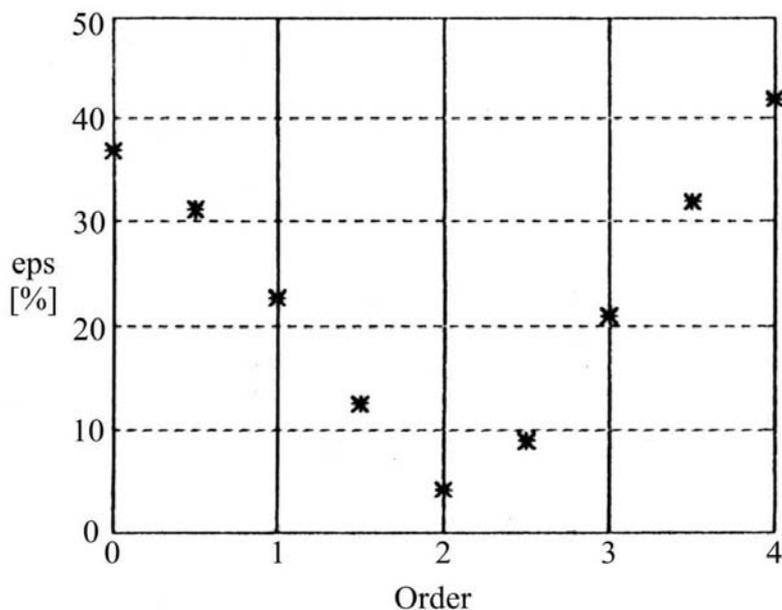


Fig. 6 – Variation of maximum relative error, in percents, versus reaction order for 55°C isotherm of a  $\gamma$  irradiated  $Na_2WO_4 \cdot 2H_2O$  polycrystalline sample.

For reaction orders verifying and determination of rate constants, corresponding to radicals thermal disappearance, it was used the differential method, too. With this purpose was used the differential kinetic equation  $-dI_r/dt = kI_r^n$ .

In Figure 7 is plotted the logarithm rate of radicals disappearance at 55°C versus logarithm relative intensity of EPR signals.

The results obtained by integral and differential methods are concordant, as follows: by integral method, the determined reaction order was 2, the rate constant was  $5,12 \cdot 10^{-3} \text{ s}^{-1}$  and by differential method, the reaction order was 2,15, the rate constant was  $5,2 \cdot 10^{-3} \text{ s}^{-1}$ .

In Table 2 are presented the kinetic parameters corresponding to radical species disappearance at different temperatures.

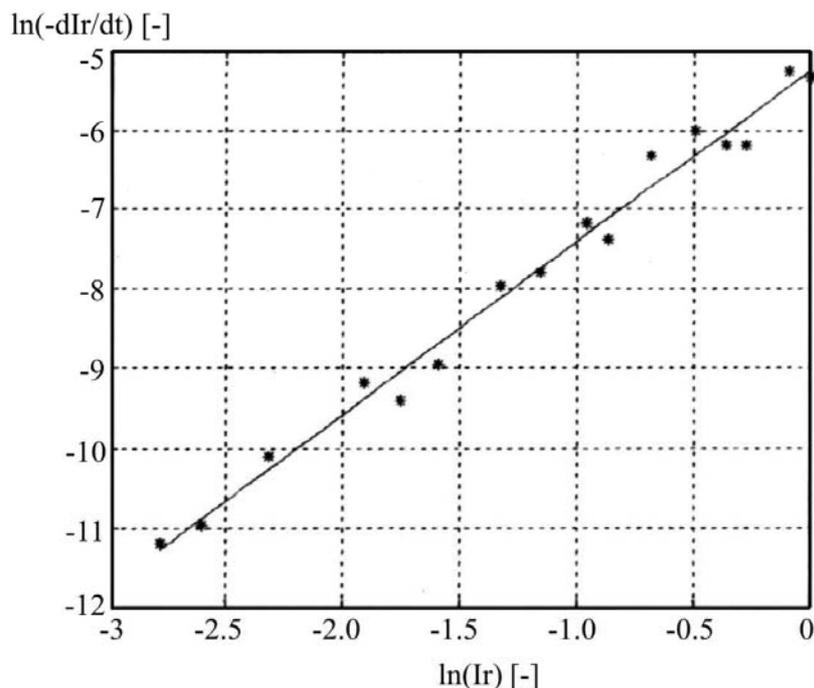


Fig. 7 – Variation of logarithm rate of radicals disappearance versus logarithm relative intensity of EPR signals ( $I_r$ ) at 55°C temperature, for a  $\gamma$  irradiated  $Na_2WO_4 \cdot 2H_2O$  sample.

Table 2

Values of reaction orders (n) and rate constants (k) for radical species disappearance at different temperatures

| Reaction order<br>"n" | t [°C] | T [K]  | 1/T [K <sup>-1</sup> ] x 10 <sup>3</sup> | k [s <sup>-1</sup> ] x 10 <sup>3</sup> | lgk + 3 |
|-----------------------|--------|--------|--|--|---------|
| 3                     | 52     | 325,15 | 3,0755                                   | 0,724                                  | - 0,14  |
| 2                     | 55     | 328,15 | 3,0473                                   | 5,12                                   | 0,71    |
|                       | 57     | 330,15 | 3,0289                                   | 10,6                                   | 1,03    |
| 0,5                   | 60     | 333,15 | 3,0016                                   | 9,22                                   | 0,96    |
|                       | 62     | 335,15 | 2,9837                                   | 17,98                                  | 1,25    |

As may be seen from Table 2, the process of radicals recombination takes place on a small temperature interval (10°C). Within this interval it will be produce the step-by-step reaction order decrease beginning from 3 to 0,5, at the same time with temperature and rate constant increase.

The decrease of reaction order on small temperature intervals did not allow the determination of rate constants at several temperatures for the same order. For orders 2 and 0,5 the activation energies of 328,4 kJ/mol and 310,06 kJ/mol, respectively, have been calculated. The values of these activation energies are very high, because the rate constants have just doubled on a two degrees interval.

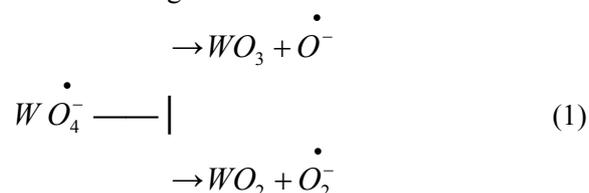
The decrease of reaction order with temperature means a general behavior, because this comportment was noticed even at the disappearance of radical species formed by other oxyanions with Cr<sup>12</sup>, Se<sup>13</sup>, Te<sup>14</sup> radiolysis.

This behavior has the following explanation: paramagnetic centres radiolytic formed are trapped in the crystalline lattice and they have different binding energies depending on the everyone position related to neighbors who interact with them. By temperature increase, the vibration energy around the equilibrium positions will rise, the binding forces which maintain radicals trapped in lattice will be weaken and finally, the mobility of radicals will increase. At high temperature even the strongest trapped radicals become mobile. In this way it can explain the change of reaction order along with the decrease of radical species concentration.

The process of  $\left(W_2 \dot{O}_8\right)^{3-}$  radicals recombination, with non paramagnetic entities formation, implies many reactions which take place simultaneously on different ways. The decrease of reaction order from 2 to 0,5 with temperature increase, proves that some reactions become predominant on a small temperature interval, determining the global order, experimentally found. This result indicates an

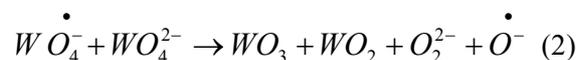
intricate mechanism, which contains several reactions of  $W \dot{O}_4^-$  species disappearance.

1. Decomposition of  $W \dot{O}_4^-$  species with oxygen ejection and tungsten oxides formation:

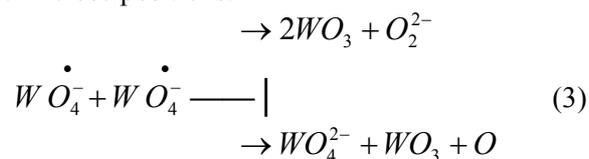


The formation of oxygen after heating of  $\gamma$  irradiated samples was chromatographic determined.

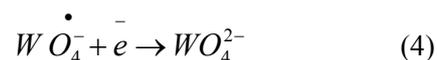
2.  $W \dot{O}_4^-$  radicals receive mobility by heating and after that, react with adjacently  $WO_4^{2-}$  and change over into non-paramagnetic species.



3. Recombination of two  $W \dot{O}_4^-$  radicals, which are in close positions.



4. Electrons trapped in crystalline lattice become mobile by heating and they could be trapped by the  $W \dot{O}_4^-$  to remake the initial ion.



## CONCLUSIONS

The radiolysis at room temperature in polycrystalline solid state of  $Na_2WO_4 \cdot 2H_2O$  was performed. The recording of irradiated

samples EPR spectra allowed the identification of  $\left(W_2 \dot{O}_8\right)^{3-}$  stable radical at room temperature.

From the kinetic study it was observed that reaction order of thermal annealing process decreases from 2 to 0,5 with temperature increasing. It was developed a mechanism of radicals radiolytic formation and radicals thermal annealing, in agreement with the kinetic study.

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