Radiolysis of Potassium Picrate in 77 K

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Abstract. The formation of paramagnetic centers in potassium picrate under irradiation at low temperature was investigated. The heating irradiated at 77 K potassium picrate crystal to room temperature results in paramagnetic centers - 2,6-dinitro-para-quinone radicals, ortho- and para-iminoxyl radicals and atomic oxygen. These products are formed under irradiation at room temperature.

1. Introduction

Potassium picrate (hereinafter PP) – nitroaromatic compound $C_6H_2(NO_2)_3OK$, being power explosive. Moreover it can undergo to all kinds of slow solid-phase decomposition under constant influence of the external power factor, such as heat, light, radiations, electromagnetic fields [1-4]. The goal of present investigation is to study the formation and transformations of the paramagnetic centers formed in PP at low-temperature irradiation.

2. Experimental

Polycrystalline PP was prepared by neutralization of a hot picric acid solution with a solution KOH. Reagents used were analytical reagent grade. PP single crystals were prepared by slow evaporation hot (60 °C) water solutions. They sizes was 15×3×4 mm and of 20-30 mg weight.

The crystals were irradiated by with ^{60}Co γ-rays at 77 K and 307 K. The dose rate was 0.16 Gy/s. The dose absorbed by the sample was calculated using the mass energy absorption coefficients.

Low-temperature annealing of the irradiated crystals of PP was made in a cryostat in a range 77-300 K with accuracy ±2K.

The ESR spectra of the irradiated crystals were recorded on a ''Rubin'' X-band ESR spectrometer at 77 and 300 K. At 77 K the crystal was immersed in liquid nitrogen contained in the finger of a Dewar. For absolute g-value determinations a calibration using DPPH (g = 2.0036) was used. The magnetic properties of studied centers were derived from series of experimental ESR spectra corresponding to rotations of the samples in three perpendicular planes in the static magnetic field.

The spin concentrations of the paramagnetic centers formed in irradiated samples were determined by comparing the intensities of the doubly integrated spectra with those obtained from reference sample – $CuCl_2{\cdot}2H_2O$ (the error in spin concentration is ±10%). To minimize experimental errors, the same condition of registration was used for all ESR measurements. The interpretation of ESR spectra was carried out according to standard procedures [5, 6].

3. Results and discussion

Figure 1 displays ESR spectrum of the γ-irradiation of potassium picrate single crystals at 77 K. Wide (1,45 mTl) isotropic asymmetric singlet with not resolved HFS was observed. When stored for 1 day its intensity do not change. Variation orientation of a single crystal concerning a magnetic field direction results in the change of the signal form, but resolution of a singlet line into separate components is not observed. A change of g-factor values was not revealed because of asymmetry of a singlet and its large width. Increasing magnetic field strength results in increasing signal intensity with slight change of the line shape. Probably this paramagnetic center (PC-0) is a combination of several defects stable at 77 K with different sensitivity to changes of the magnetic field. Thus, to identify the nature of the center based on the spectroscopic parameters it is extremely difficult. Therefore, to clarify its nature, it is necessary to carry out additional investigations.

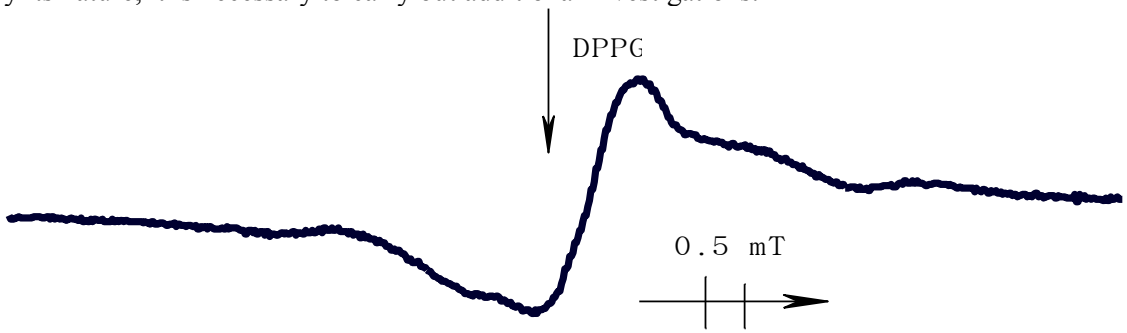

Figure 1. The ESR spectrum of the PP irradiated to 69 kGy at 77 K

The γ-irradiation of single crystals of PP at room temperature results in ESR-signal with HFS [1] is due to presence of four paramagnetic centers (figure 2):

PC-1 – The anisotropic triplet with splitting 0.15 – 0.53 mTl and the intensity ratio 1:2:1; has been identified as a 2,6-dinitro-p-quinone radical formed at eliminating on NO molecule from picrate-anion;

PC-2 – Two nonequivalent triplets, apparently, iminoxyl-radical formed at break off of oxygen from nitro-group in an ortho-position;

PC-3 – The isotropic singlet in half-width 0.25 mTl, it is presumably due to O^-;

PC-4 – The singlet with half-width 0.55 mTl, is preliminarily identified as a radical with nitro-group in para-position in a benzene ring.

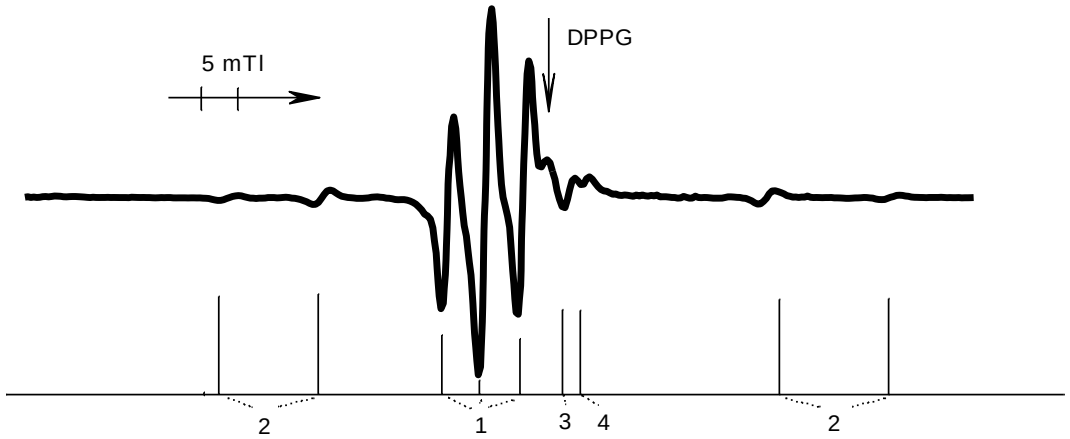

Figure 2. The ESR spectrum of the PP, irradiated to 238 kGy at room temperature: 1 – PC-1, 2 – PC-2, 3 – PC-3, 4 – PC-4

The spectroscopic parameters of paramagnetic centers in γ-irradiated at room temperature potassium picrate crystals [7] are given in table 1.

PC-1, PC-2 and PC-3 are stable at room temperature. When stored for 1 day the line intensity of PC-4 decreases slowly.

Table 1. ESR spectroscopic parameters of paramagnetic centers in γ-irradiated potassium picrate crystals.

Parameter	Paramagnetic center				
	PC-0	PC-1	PC-2	PC-3	PC-4
T_{xx} (mTl)	–	0.199	1.214	–	–
T_{yy} (mTl)	–	-0.291	-0.205	–	–
T_{zz} (mTl)	–	-0.205	-0.705	–	–
g_{xx}	2.0033	2.0086	2.0098	2.0028	20032
g_{yy}	2.0033	2.0046	2.0045	2.0028	2.0032
g_{zz}	2.0033	2.0019	2.0018	2.0028	2.0032
A_{iso} (mTl)	–	-0.342	3.125	–	–
ΔH_{max} (mTl)	1.450	0.150	0.245	0.550	0.250
ρ	–	0.127	–	–	–

The heating from 77 K to room temperature result in irreversibly and completely decay of the PC-0. From 77 to 100 K the signal intensity decreases sharply, further to 140 K - is not actually changing. At the temperature range 230-235 K the signal was vanished almost instantly and there is no new ESR signal is appeared.

When storing irradiated at 77 K PP crystal at room temperature during 1 hour, ESR signal is appeared again. It is identical to the PC-1 and PC-3 that in γ-irradiated at 307 K PP. During storage, the PC-1 concentration increased, tending to saturate for 24 hours. The maximal concentration is equal to (within experimental error) with that of PC irradiation at 307 K with the same dose of radiation (figure 3).

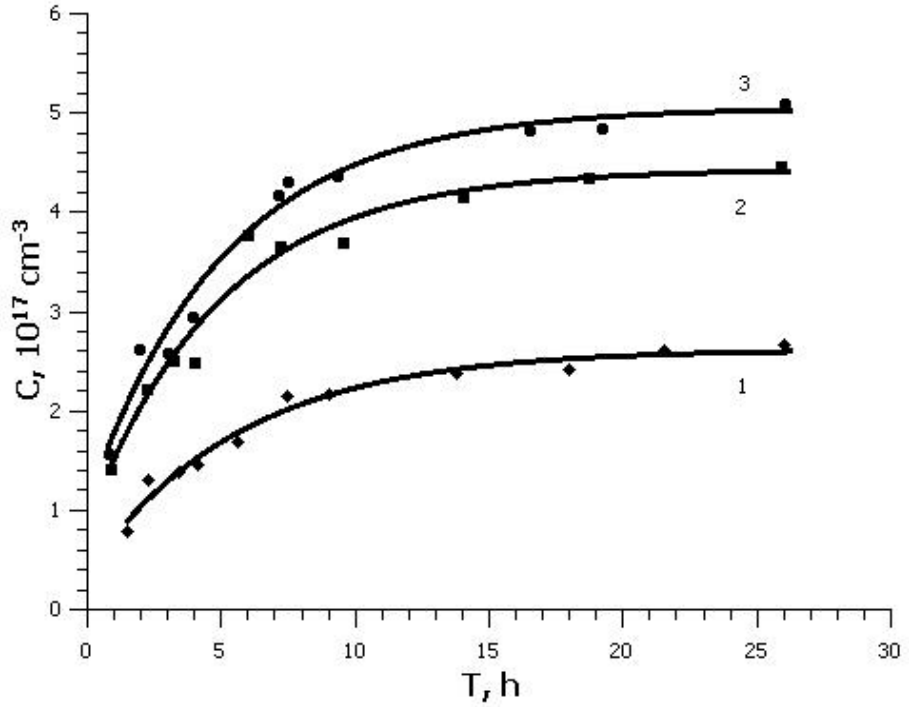

Figure 3. The accumulation of the PC-1 at different doses (1 – 30 kGy, 2 – 75 kGy, 3 – 98 kGy)

At the absorbed dose above 100 kGy, intensity ESR signal sharply increased and is displayed HFS signal PC-1. The analysis of spectroscopic characteristics displayed that a HFS is caused by a appearing iminoxyl radical in an ortho- and para-positions (figure 4).

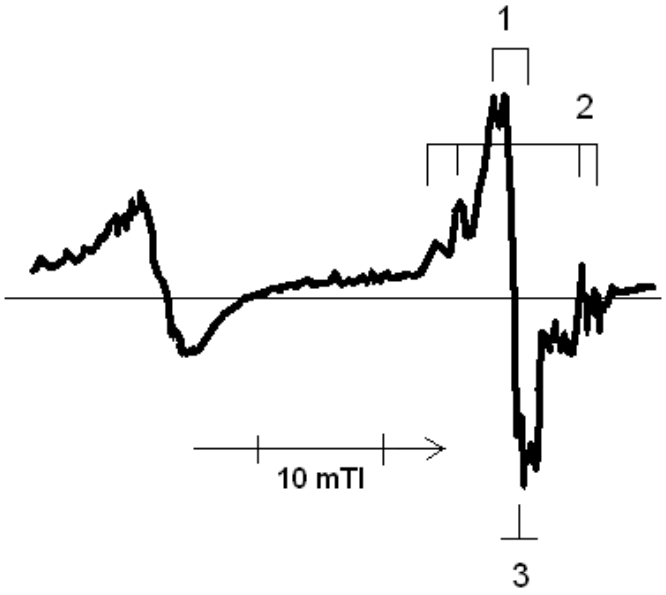

Figure 4. The ESR spectrum of the PP, irradiated to 453.2 kGy: 1- iminoxyl radical in a para-positions, 2 - iminoxyl radical in an ortho-positions, 3 - 2,6-dinitro-p-quinone radical.

Experiment of low temperature annealing showed that the nature of thermal decay of the paramagnetic centers in crystals PCs irradiated γ-rays to a dose of 300 kGy, is very different. ESR signal intensity of PC-1 in the range of 80-150 K decreases almost 10 times (figure 5), after remaining constant up to room temperature. The intensity of the EPR signal of PC-2 is reduced gradually. For PC-3 signal characteristic nonmonotonic change - at first it slowly increases, then gradually decreases (figure 6)

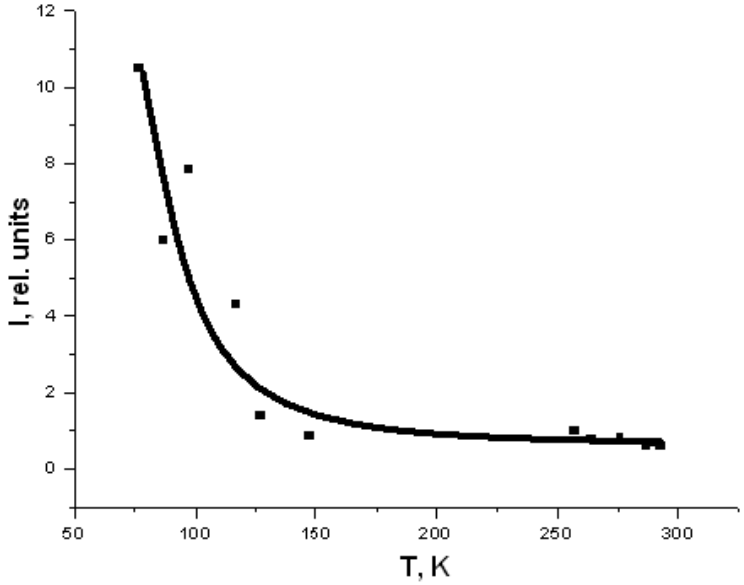

Figure 5. The temperature dependence of ESR signal intensity of PC-1

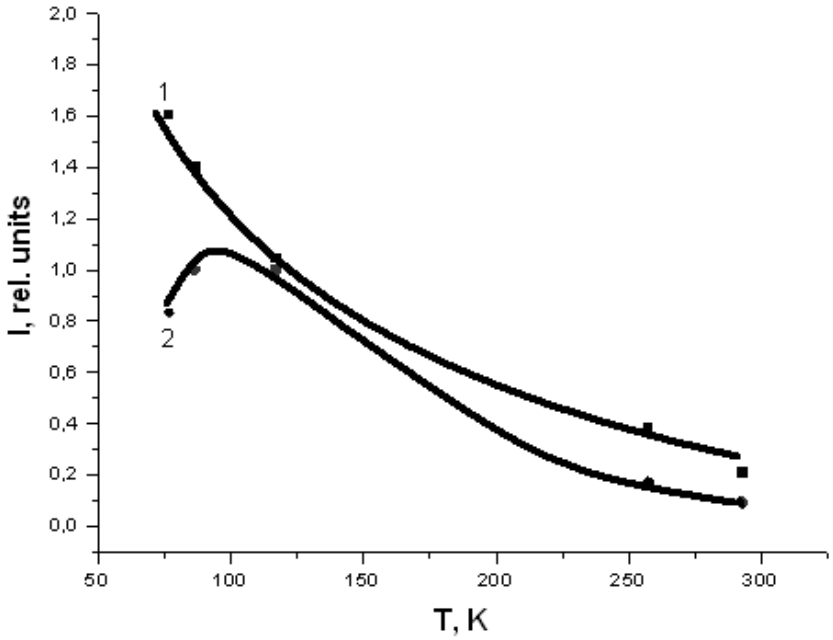

Figure 6. The temperature dependence of ESR signal intensity PC-2 (1) and PC-3 (2)

The obtained experimental data indicate the complex mechanism of the formation and transformation of paramagnetic centers formed in γ-irradiation of potassium picrate at 77 K.

Acknowledgements

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