The Paramagnetic Centers In Potassium Picrate

V.Kh. Pak, S.M. Ryabykh, D.G. Yakubik

Kemerovo State University, Ul. Krasnaya, 6, Kemerovo, 650043, Russia

Abstract – In the present work results of researches of formation, and transformations of the paramagnetic centers arising in PP at an irradiation are described.

1. Introduction

Potassium picrate (PP) – nitroaromatic compound $C_6H_2(NO_2)_3OK$, being power explosive. Besides explosive, it is capable to undergo all kinds of slow solid-phase decomposition at constant influence of the external power factor (warmly, light, radiations, electromagnetic fields) and consequently is of interest for physics and chemistry of solids as modeling system. The research carried out in our laboratory have shown, that the paramagnetic centers formed at an irradiation of PP have unique heat stability (down to T=360 K), and their concentration reaches $10^{19} g^{-1}$.

In the present work results of researches of formation, and transformations of the paramagnetic centers arising in PP at an irradiation are described.

2. The experimental technique

Initial polycrystalline PP obtained at neutralization of a hot solution of picric acid by solution KOH. At achievement pH=7 the fine-crystalline precipitate of yellow color dropped out. A precipitate washed out cool water and ethanol. Utilized reagents had the mark "clear". Single crystals of PP grew slow evaporation hot (60 ^{0}C) water solutions. In some day the single crystals, shaped needles with the sizes up to 15×3×4 mm and weight of 20–30 mg dropped out. The irradiation was carried out{was spent} by γ-quantums ^{60}Co on installation RChM-γ-20 and high-velocity electrons with energy ~150 keV on plant of the MIRA-2D. Capacity of an absorbed doze has made 1,4–2,8 Gr/s for γ-radiation and $7*10^3$ Gr/s for high-velocity electrons. An irradiation carried out on plant RChM-γ-20 at temperature (307 K) the central channel and at temperature of liquid nitrogen, and at room temperature high-velocity electrons on the pulse accelerator (MIRA-2D). Low-temperature annealing of the irradiated crystals of PC carried out in a cryostat in a range 77–300 K with accuracy ±2K. Spectrums the ESR registered on a radiospectrometer such as "Ruby" with frequency of modulation of 100 kHz at room temperature and 77 K.

3. ESR spectrums of potassium picrate crystals irradiated at room temperature

The irradiation of single crystals of PP in γ-quantums at 307 K and high-velocity electrons at room temperature generates a complex ESR-signal having hyperfine structure (HFS) which is given in Fig. 1

The observable ESR spectrum is caused by presence of four paramagnetic centers (PC). PC-1 – an anisotropic triplet with splitting of 0,15–0,53 mTl and a ratio of intensities 1:2:1. PC-2 – two nonequivalent triplets, PC-3 – an isotropic singlet in width of 0,25 mTl. PC-4 – a singlet in width of 0,55 mTl. Spectroscopic parameters PC are given in the table.

The centers 1,2,3 at room temperature are stable, concentration PC-4 during 1 day of storage slowly decreases.

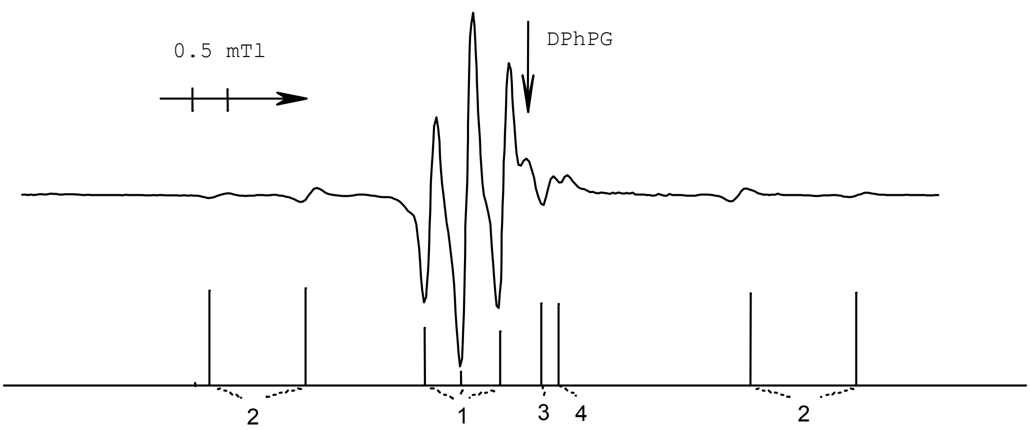

Fig. 1. A spectrum ESR γ – the irradiated PC at orientation H || of an axis *b* a single crystal at temperature 298 K (a doze 2 MGr). By figures 1–4 are designated paramagnetic centers the various nature.

The paramagnetic center – 1. The HFS arises at interaction of not coupled electron, delocalyzed on a benzene ring, with two equivalent protons in meta-position, hyperfine interaction with nucleus 14N a nitro-group insignificantly, it results in change of the form of a line at various orientations of a single crystal. PC-1, earlier we had been identified as a radical 2,6-dinitro-p-quinones, formed at eliminating from picrate-anion NO.

Spectroscopic parameters PC-1 are given in the table. Value of the spin density obtained from a McConel's ratio (Q = 2,71 mTl) – 0,127.

The paramagnetic center – 2. On the basis of comparison of obtained spectroscopic characteristics with literary data PC-2 it is presumably identified as an iminoxyl-radical formed at a separation of oxygen from nitro-groups in ortho-position.

Besides the ESR is present at a spectrum other triplet with a intensities ratio 1:1:1, apparently, belonging to a iminoxyl-radical in para-positions. In details it was not investigated because of low concentration (0,4 from concentration PC-2).

The paramagnetic center – 3. The spectrum ESR PC-3 represents an isotropic singlet (g = 2,0028) with ΔH_{max} = 0,25 mTl. At change of registration temperature up to 77 K the insignificant enlargement of a ESR-signal is observed. To attribute the signal to colloidal potassium particles it is impossible, because PC with similar behavior and similar spectroscopic parameters it is found out by us in the irradiated crystals of picric acid, sodium picrate and lead styphnate. On analogies to the data obtained for alkali metal nitrates, this center it is identified by us as a radical O^-.

The paramagnetic center – 4 – a singlet in width of 0,55 mTl. At room temperature it is unstable, its concentration slowly decreases during the order of 20 hours up to not registered value. In Fig. 2 spectrum PC-4 obtained immediately after an irradiation of PP by pulses of high-velocity electrons is shown. PC-4 it is identified as a radical containing nitrite-group in para-positions of a benzene ring.

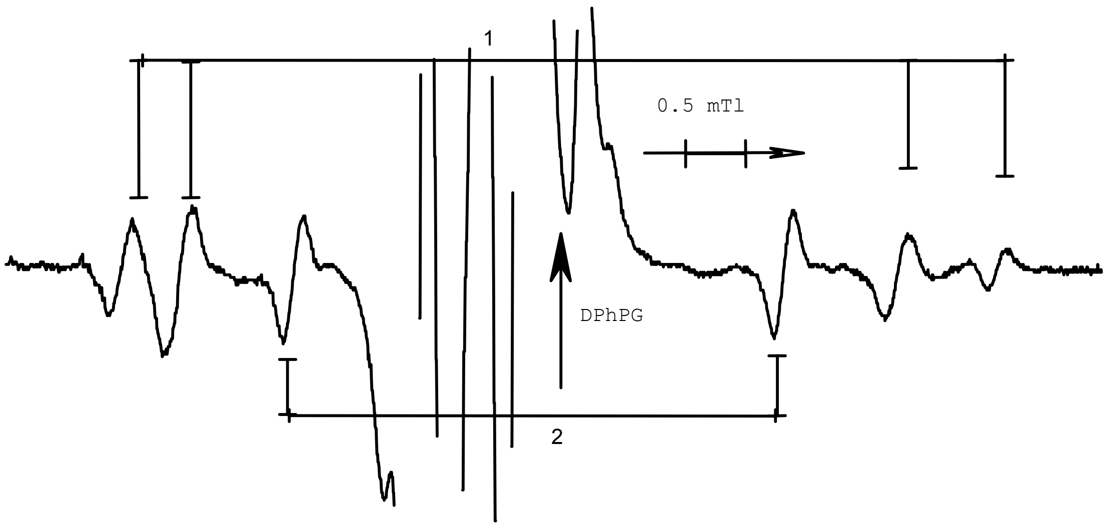

Fig. 2. A ESR spectrum of iminoxyl-radicals (PC-2). 1 – an iminoxyl-radical in ortho-position; 2 – an iminoxyl-radical in para-positions. Center lines belong to anothers PC.

Table. Spectroscopical parameters paramagnetic centers in the irradiated potassium picrate

PC	T_{xx}, mTl	T_{yy}, mTl	T_{zz}, mTl	g_{xx}	g_{yy}	g_{zz}	A_{iso}, mTl	ΔH_{max}, mTl	ρ
0	----	----	----	2,0033	2,0033	2,0033	----	1,450	----
1	0,199	-0,291	0,090	2,0086	2,0046	2,0019	-0,342	0,150	0,127
2	1,214	-0,205	-0,705	2,0098	2,0045	2,0018	3,125	0,245	----
3	----	----	----	2,0028	2,0028	2,0028	----	0,550	----
4	----	----	----	2,0032	2,0032	2,0032	----	0,250	----

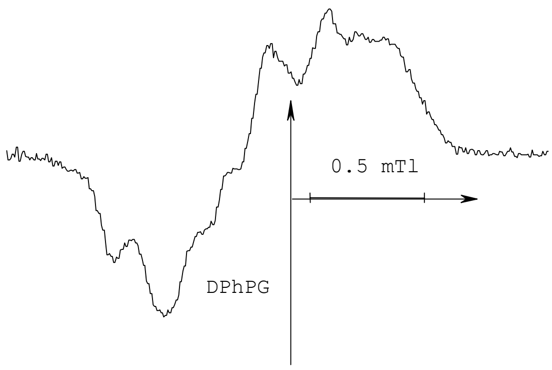

Fig. 3. Spectrum PC-4 obtained immediately after an irradiation of PP pulses of high-velocity electrons at temperature 298 K.

4. Spectrums the ESR of picrate of the potassium irradiated at 77 K

The irradiation of single crystals of PC in γ-quantums and pulses of high-velocity electrons at 77 To generates an ESR-signal submitted in Fig. 3. It is wide (1,45 mTl), an isotropic asymmetric singlet with the unresolved HFS.

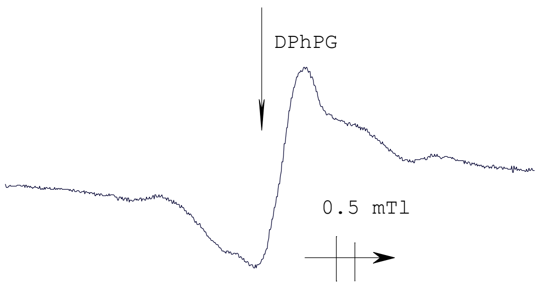

Fig. 3. A spectrum the ESR irradiated at temperature 77 K PP (orientation H ││ of an axis *b* a single crystal)

At change of orientation of a single crystal concerning a direction of a magnetic field change of the form of a line of the given singlet but what – or resolutions of a singlet to separate components is not observed is observed. What or apparent changes of g-value – the factor it was revealed not because of asymmetry of a singlet and its big width. At increase in microwave capacity propagation of intensity of all spectrum with weak change of the form of a line is observed. Change of the form of a line specifies formation in a field of radiation of several types of defects, stable at 77 K, with various sensitivity saturation by microwave-capacity. Thus, to identify given paramagnetic center (PC-0 or ensemble PC) on spectroscopic parameters appeared the extremely problematic, therefore its nature is considered from the analysis on accumulation PC at 77 K and low-temperature annealing.

At defreezing from 77 K up to room temperature PC-0 it is irreversible and completely perishes at critical temperature 230–235 K. Ac T signal strength varies a little, and at achievement T the signal disappears practically instantaneously. Thus there is no new signal the ESR. However, during storage irradiated at 77 K a crystal at 298 K in 1 hour per it the ESR-signal completely identical PC-1 and PC-3 in case of an irradiation at 317 K again is registered. During storage concentration PC-1 grows, amounting to saturation within 24 hours. Maximal concentration PC-1 within the experimental error limits is equal same if to irradiate PC at 317 K the same doze.

The kinetic curve of accumulation PC-1 has an interesting kind at a discontinuous irradiation in the field of small dozes as it is shown in Fig. 4. After the ending an irradiation concentration PC-1 continues to increase, and during approximately of ten hours reaches stationary value; the relative increase in concentration during an exposure in inverse proportion to an absorbed doze, and at dozes more than 200 kGr size of this effect lays within the limits of an experimental error. The given effect can be observed repeatedly. At the subsequent irradiation reduction of concentration PC-1 up to value which would be observed if the irradiation would be continuous is take placed.

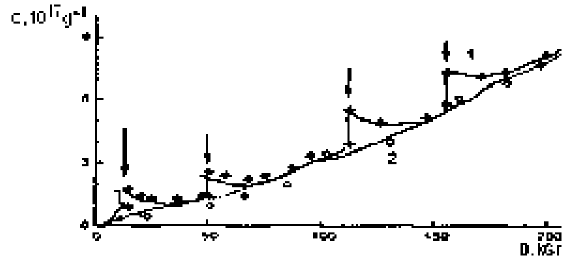

Fig. 4. 1 – Kinetics of change of concentration of a radical 2,6-dinitro-p-quinones in potassium picrate at a discontinuous irradiation and temperature 298 K (arrows designate the moments of termination / beginning of an irradiation), a pause of 5 hours. 2 – Concentration of a radical 2,6-dinitro-p-quinones at a continuous irradiation at 298 K

At an irradiation the pulse radiation source, allowing to reach the big radiation dose for the period of time about several minutes, during the dark pause on a background of spectrum PC-4 spectral lines the ESR of a radical 2,6-dinitro-p-quinones are appeared, their intensity increases, while intensity of singlet PC-4 decreases up to not registered value. Apparently, destruction PC-4 occurs and during an irradiation but as time of an irradiation γ-radiation makes some hours we observe only a final stage of this process.

Thermal stability PC-1 has been investigated in a range 293 – 506 K. Storage at room temperature of the PP irradiated with γ-radiation at 317 To result in increase of concentration PC-1, Concentration of PC-1, as well as in the previous case, aspires to saturation.

After obtaining of concentration of saturation concentration PC-1 remains constant at storage at room temperature at least 6 months. At a heating-up with constant speed, PC-1 is stable down to 360 K. By the further rise in temperature its concentration are falls, the center completely disappears at T > 500 K. Therefore studying of destruction PC-1 kinetics was made at the fixed temperatures in a range 423–506 K. Corresponding kinetic curves are given in Fig. 5. Thermal destruction PC-1 occurs under laws polychronic kinetics and, apparently, is caused by recombination of a genetic radical pair.

In our opinion the radical 2,6-dinitro-p-quinones is a product of decay PC-4

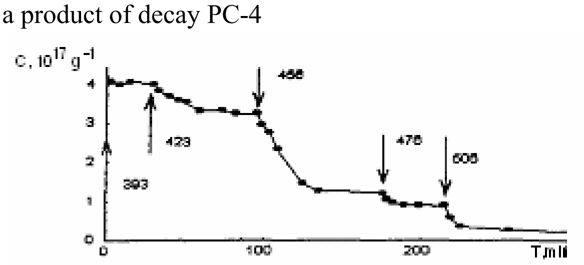

Fig. 5. Stepped kinetics of a radical 2,6-dinitro-p-quinones destruction in γ-irradiated at room temperature of potassium picrate (a doze 1,2 MGr). Arrows show the beginning of warmup at the given temperature in T_o

At defreezing from 77 K up to room temperature PC-0 it is irreversible and completely perishes at critical temperature 230–235 K. From 77 up to 100 K signal strength sharply drops further up to 140 K and actually does not vary, whereupon the signal disappears practically instantaneously. Thus there is no new ESR-signal. However, during storage irradiated at 77 K a crystal at 298 K through approximately 1 hour per it again is registered a signal an ESR completely identical PC-1 and PC-3 in case of an irradiation at 307 T_o. During storage concentration PC-1 grows, amounting to saturation within 24 hours. Maximal concentration PC-1 within the limits of an experimental error is equal same if to irradiate PC at 307 K with the same doze. The interesting kind has a spectrum the ESR of potassium picrate at an irradiation at 77 K in the field of dozes more than 100 kGr as it is visible in Fig. 6. With increase in an absorbed doze all is more distinctly appeared HFS of paramagnetic centers. The analysis of spectrums shows, that HFS is caused by an iminoxyl-radical in an ortho- and para-positions, and also PC-1 which in this case has the form of a wide singlet. At the further irradiation the increase in intensity of lines PC-1 is observed and PC-2 is similar to doze accumulation at room temperature. At the same dozes there is a doublet of lines with splitting in 50 mTl referred by us to a radical of singlet hydrogen.

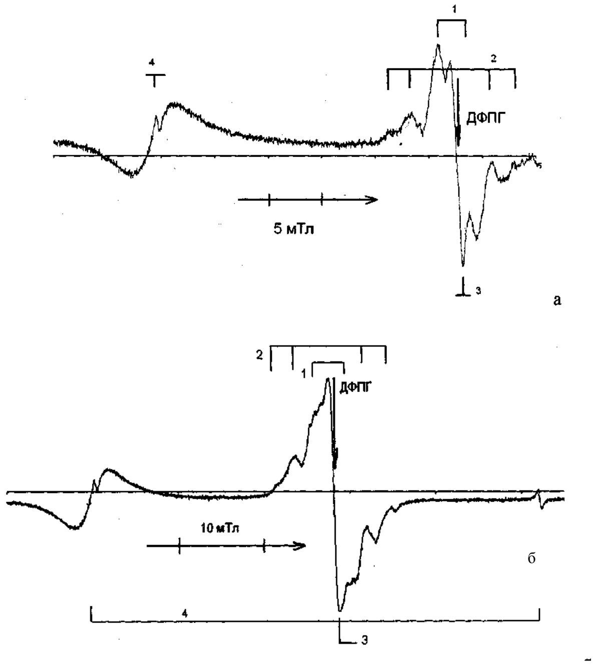

Fig. 6. A spectrum the ESR of the PP irradiated up to: a) 238 kGr, b) 396 kGr. 1 – an iminoxyl-radical in para-positions; 2 – a iminoxyl-radical in ortho-position; 3 – radical of 2,6-dinitro-p-quinone; 4-hydrogen radical

For iminoxyl-radicals the spin density is allocated approximately fifty-fifty between nitrogen and oxygen, thus the significant part of it is on 2s-orbital of nitrogen, i.e. HFS with nitrogen atom will have the significant isotropic contribution., as it is observed in spectrums. As is known, the iminoxyl-radical is formed at a separation of oxygen from NO_2 in ortho-position concerning a hydroxyl group

5. Conclusion

Obtained experimental material allows to put forward quite proved schema of processes with participation PC. It is supposed, that PC 1–4 are formed as a result of a molecular exciton decay on heavy and easy fragments. From a molecular exciton basically can be eliminated as easy fragments NO_2, O-, NO, and heavy fragments will be iminoxyl-, quinone- and intermediate (PC-4) radicals. These processes, however are not elementary, that have shown ESR-spectra of the PC irradiated at 77 K. At this temperature the spectrum without HFS which with increase in a radiation dose is transformed to a spectrum quite resolved HFS similarly room is obtained.

It testifies to the complex mechanism of formation and transformations PC at a low-temperature irradiation of potassium picrate.