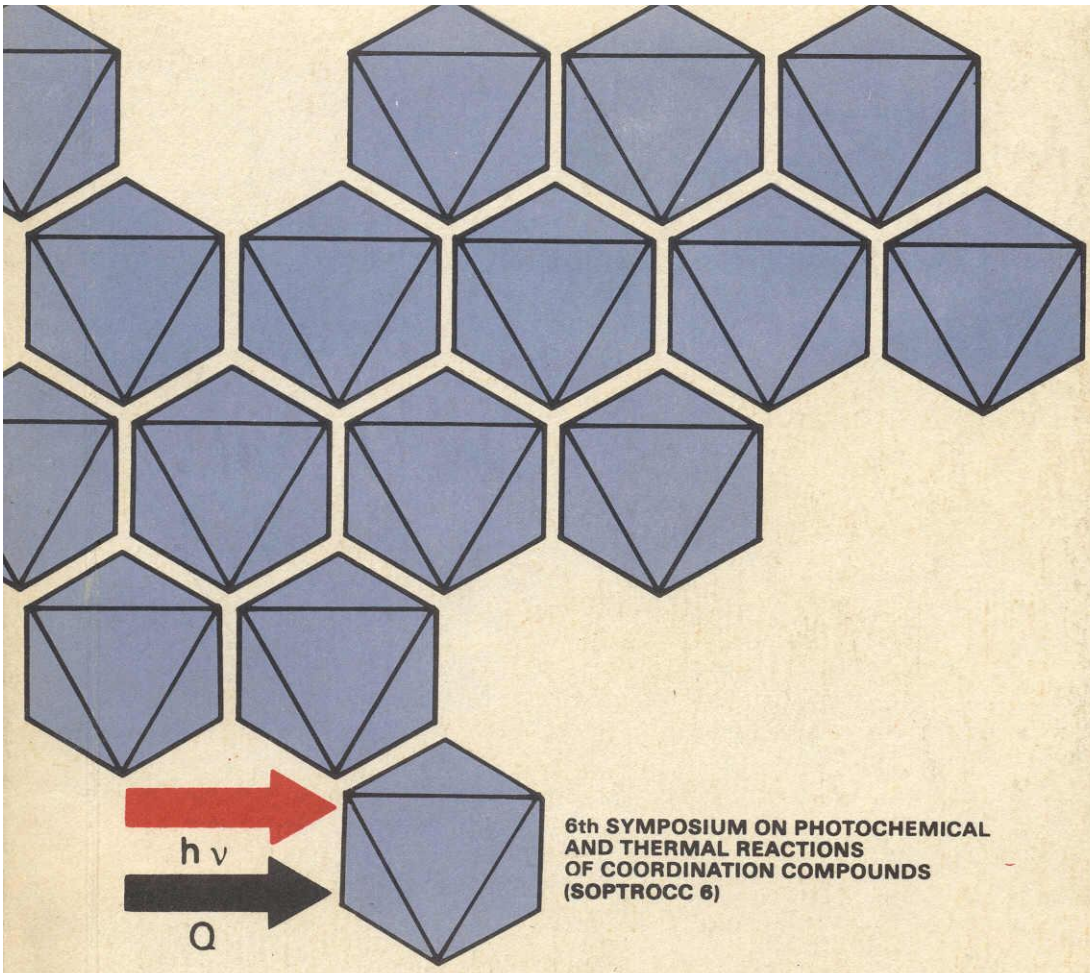

6th SYMPOSIUM ON PHOTOCHEMICAL AND THERMAL REACTIONS OF COORDINATION COMPOUNDS (SOPTROCC 6)

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SPIN TRAPPING IN THE RADIOLYSIS OF PHOSPHATE ESTERS

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Summary: Radicals formed at X- and gamma radiolysis of glass and liquid phosphate esters and dibutylbutylphosphonate were studied by the spin trapping technique using C-phenyl-N-tert.-butylnitrone (PBN) and 2-methyl-2-nitrosopropane (MNP) as the spin trap agents. Nitroxyl radicals generated by the spin trapping of hydrogen atoms and of the labile radicals of phosphates or phosphonate using PBN were identified after irradiatian in vacuum. Radiation-chemical yield of spin adducts and the free activation energy of the spin adducts decay were observed. Mechanism of generation and decay of nitroxyl radicals is discussed. The spin adducts with MNP have a relatively low stability and superposition of some adducts is observed.

It has been proved by the low-temperature X-radiolysis of alkylphosphates with the use of electron spin resonance (e.s.r.) spectroscopy[1] that primarily radicals with the $CH_3\dot{C}HCH_2$- fragment are formed and they react in the presence of oxygen to form peroxy radicals. A radical with the $-O-C_6H_4-\dot{C}H_2$ fragment is formed in the case of tributylphosphate whose aromatic nucleus participates in the delocalization of the unpaired electron. Both types of radicals decay at room temeperature. Therefore, further study of radicals in the liguid phase was carried out using the spin trap agents - PBN and MNP.

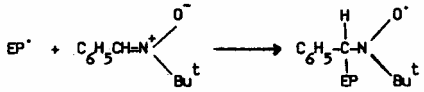
The aim of this study was to find the character of radical products formed at X- and gamma-radiolysis of technically used extragents: tri-n-butylphosphate (TBP), di-n-butylphosphate (DBP), di(2-ethylhexyl)phosphoric acid (DEHPA) and perspective extragents tri-p-tolylphosphate (TTP) and di-n-butyl-n-butylphosponate (DBBPN) by means of the PBN and MNP spin trap agents.

0.1-0.3 mol dm^{-3} deaerated solutions of the spin trap agent in corresponding phosphate (phosphonate) were used for irradiation. For X-irradiation the BCHV-7 X-ray tube was used (40 keV, I=80 mA, USSR). The methanol with 4 % of water was used[1] as a dosimeter (dose rate 2.9 Gy s^{-1}). The dose rate for gamma-radiation (^{60}Co, Fricke dosimeter) was 0.49 Gy s^{-1}. The e.s.r. spectra were registered by the e.s.r. spectrometer RE 1307 (USSR) and ERS 230 (GDR) in the X-band with a high-frequency modulation of 100 kHz in both cases.

The spin adducts were of low stability and superposition of several radical adducts e.s.r. spectra was observed using MNP as the spin trap agent. Superposition of least two radicals spectra is evident at the X-radiolysis of MNP solutions in TBP, DEHPA, TTP or in DBBPN. Superposition was also observed at the gamma-radiolysis of the MNP solution in DEHPA.

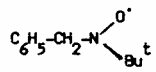
Radical adducts characterized by the triplet of doublets at room temperature are formed by the addition of radiation-generated labile radicals[1] of TBP, DEHPA and DBBPN to the spin trap agent. A triplet is observed in the case of the irradiation of DBP or TTP together with PBN at 293 K due to the high viscosity of phosphate. The typical triplet of doublets is observed only at higher temperature (323-363 K).

The iminoxyl structure of these radical adducts is expected (where phosphate ester = EP)



The hyperfine splitting (hfs) constants and g-factors of adducts are presented in Table.

Several minutes after irradiation of TBP or DBBPN some slightly intensive lines at the edge of the spectrum and among the intensive ones are observed and assigned to the spin adduct of the hydrogen atom with PBN.



The spin trap adducts with PBN are sufficiently stable (nitroxyl radicals EP-PBN$^{\cdot}$) and their concentration can be measured from several hours to several days. The dependence of the thermal decay of spin adducts in coordinates for second order reactions and there is disagreement with this relationship. Good linear dependences were achieved in the coordinates for the first order reactions. The rate constant k_1 and the half-time of decay $\tau_{1/2}$ were calculated from the slope of the lines. Free activation energy of the spin adducts decay at 293 K was also calculated[2].

Table. Characteristics of the e.s.r. spectra of nitroxyl radicals after the irradiation of phosphate esters wit PBN, their radiation-chemical yield, the half-time and free activation energy of the spin adducts decay.

Ester	g-factor	Constants of hfs (mT)			$\Delta H_{1/2}$ (mT)	G(R$^{\cdot}$)[a]	$\tau_{1/2}$ (hr)	$\Delta G^{\neq}$ (kJ mol^{-1})
		a_N^{α}	a_H^{β}	$a_H^{\beta'}$				
TBP	2.0065	1.475	0.286	0.780	0.116	1.4	46.39±0.15	94.9±0.4
DBP[b]	2.0064	1.565	0.367		0.255	1.1	7.7±0.64	90.8±0.6
DEHPA	2.0063	1.479	0.276		0.121	0.8	84.0±2.1	96.3±0.4
TTP	2.0061[c]	1.463	0.245		0.164	0.4	139.6±6.7	97.4±0.5
DBBPN	2.0032[d]	1.505	0.297	0.774	0.131	0.5	35.28±0.08	94.3±0.4

[a] radicals/100 eV; [b] at 323 K; [c] at 343 K; [d] at 363 K.

1. J. Kuruc, V.E. Zuberev, L.T. Bugaenko anf F. Macášek, J. Radioanal. Nuclear. Chem., Letters, in press.

2. A. Gordon, R. Ford, Sputnik khimika, Mir, Moscow, 1976, p. 158.