

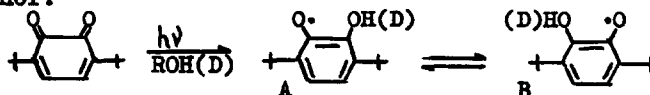
**A Kinetic Isotope Effect of the Intramolecular Hydrogen Migration within 2-Oxy-3,6-di-tert-butylphenoxy Radical.**

A.I.Prokof'ev, N.N.Bubnov, S.P.Solodovnikov, M.I.Kabachnik

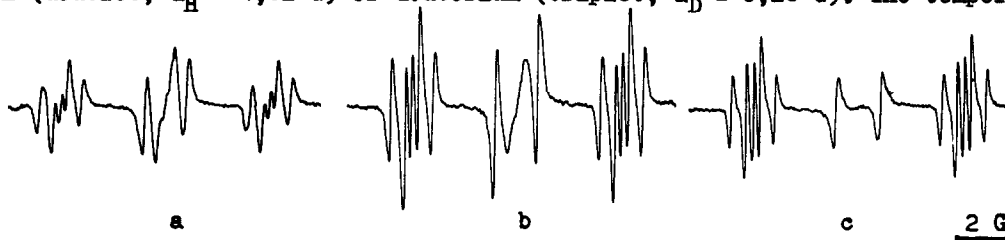
Institute of Organo-Element Compounds, Acad.Sci. USSR, Moscow, USSR.

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The 2-oxy-3,6-di-tert-butylphenoxy radical was prepared by the photolysis of the 3,6-di-tert-butyl-orthoquinone solution with 2,6-di-tert-butylphenol as hydrogen or deuterium donor:



This system is an ideal model for the isotope effect investigation on the simplest reaction of the atom migration between two equivalent states. ESR spectra of these radicals are given in the Figure. An unpaired electron interacts with two ring protons (triplet,  $a_H = 3,9$  G) and with the oxy-group proton (doublet,  $a_H = 1,62$  G) or deuterium (triplet,  $a_D = 0,26$  G). The tempera-



**Figure.** ESR spectra of 2-oxy-3,6-di-tert-butylphenoxy radical (with OH and OD groups at the same times): a- 393°K, b- 333°K, c- 273°K.

ture variation has been found among the linewidth of the triplet hyperfine lines. The linewidth alternation can be accounted for by modulation of the isotropic proton hyperfine splitting<sup>1,2)</sup> as result the intramolecular hydrogen migration between two oxygen atoms (A and B forms-).

The frequencies of proton and deuterium migration were determined at the

temperature interval 273 to 393°K, from which the activation energy and frequency factor were obtained by using Arrhenius equation

$$\nu_H = 3,3 \cdot 10^{11} \exp -(2900 \pm 200/RT) \text{ sec}^{-1},$$

$$\nu_D = 6,0 \cdot 10^{11} \exp -(4500 \pm 200/RT) \text{ sec}^{-1}.$$

The experimental frequencies at different temperatures, experimental and theoretical isotope effects ( $\nu_D/\nu_H$ ) are given in table.

The isotope effect can be described by the following approximate equation<sup>3)</sup>

$$\nu_D / \nu_H = \exp \left\{ \frac{hc}{2kT} (\bar{\nu}_{OD} - \bar{\nu}_{OH}) \right\}$$

where  $\bar{\nu}_{OD}$  and  $\bar{\nu}_{OH}$  are stretching vibration frequencies of the OD and OH bonds respectively. The stretching vibration frequency of the OH bond is found at 3600  $\text{cm}^{-1}$ ,<sup>4)</sup>  $\bar{\nu}_{OD}$  is calculated by  $\bar{\nu}_{OD}/\bar{\nu}_{OH} = (m_H/m_D)^{1/2}$  <sup>3)</sup> The agreement between theoretical and experimental values of isotope effect over the whole temperature range is good (see Table). It should be noted, that the value  $1/2(\bar{\nu}_{OD} - \bar{\nu}_{OH})$  is  $-1400 \text{ cal} \cdot \text{mole}^{-1}$ , and corresponds to the experimental value of activation barrier difference of deuterium and proton migration  $\Delta E = E_D - E_H = 1600 \text{ cal} \cdot \text{mole}^{-1}$ .

Table. Frequencies for the intramolecular migration of proton and deuterium within 2-oxy-3,6-di-tert-butylphenoxy radical. Solvent: heptane.

$^{\circ}\text{K}$	$\nu_H \cdot 10^{-9} \text{sec}^{-1}$	$\nu_D \cdot 10^{-9} \text{sec}^{-1}$	$\nu_D/\nu_H$ (exper.)	$\nu_D/\nu_H$ (theor.)
273	2,0	-	-	-
293	3,2	0,3	0,09	0,09
333	5,5	0,75	0,14	0,12
353	6,3	1,0	0,16	0,14
393	10,0	2,2	0,22	0,17

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