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EFFECT OF SUBSTITUENT AND NATURE OF SOLVENT ON ACYLOTROPY IN 3,6-DI-tert-BUTYL-2-ACYLOXYPHENOXYLS

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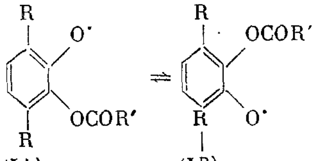
It was shown by us in a previous paper [1] that intramolecular migration of the acetyl group between the oxygen atoms is observed in 3,6-di-tert-butylacetoxyphenoxyl. The acylotropic transitions



(IA) (IB) $R = t\text{-}C_4H_9$

lead to a specific broadening of the lines of the hyperfine structure in the EPR spectra of the studied radicals, which makes it possible to estimate the kinetic parameters of these transitions. In the present paper the acylotropy phenomenon is discussed on the example of other 3,6-di-tert-butyl-2-acyloxyphenoxyls (Table 1). The EPR spectra of all of the studied radicals represent a doublet ($a_H = 10.2 \pm 0.2$ Oe) due to the coupling of the unpaired electron with the ring proton in the p-position to the phenoxyl, each component of which is split into two lines ($a_H = 1.95 \pm 0.15$ Oe) via the m-proton to the phenoxyl. A broadening of the extreme components in the EPR spectra of these radicals is observed when the temperature is raised to 120°C, which testifies to migration of the acyl groups between the oxygen atoms (Fig. 1). The indicated changes in the EPR spectra are completely reversible when the temperature is varied, and an analysis of the width of the lines made it possible to determine the acylotropy frequency (ν_{exchange}) [2]

$$\nu_{\text{exchange}} = \gamma_e \Delta\,(1/T_2)$$

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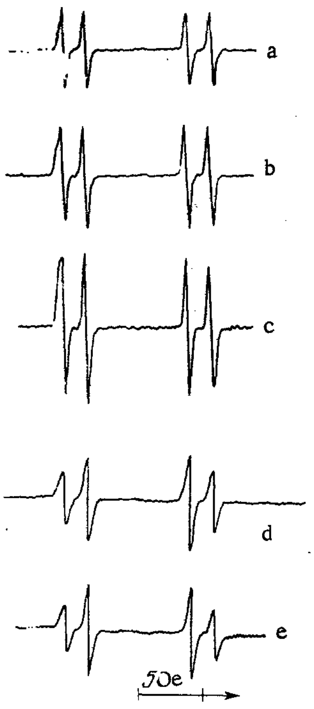


Fig. 1. EPR spectra of 3,6-di-tert-butyl-2-propionyloxyphenoxyl at various temperatures, °C: a) –20; b) 0; c) 20; d) 50; e) 70.

TABLE 1. Substituent Effect on Kinetic Parameters of Acylotropy in 3,6-Di-tert-butyl-2-acyloxy Radicals

Acyl	$\nu(20°)$, sec^{-1}	ν_0, sec^{-1}	E_{act} ± 1.0, kcal/mole
$COCH_3$	10^4	$0{,}9 \cdot 10^{13}$	11,4
COC_2H_5	10^4	$1{,}1 \cdot 10^{13}$	13,0
$COCH_2Br$	$2{,}6 \cdot 10^5$	$2{,}1 \cdot 10^{13}$	10,0
$COCH_2C_6H_5$	10^5	$0{,}6 \cdot 10^{12}$	9,15
$COCH(C_6H_5)_2$	$3 \cdot 10^4$	$2{,}3 \cdot 10^{12}$	10,7

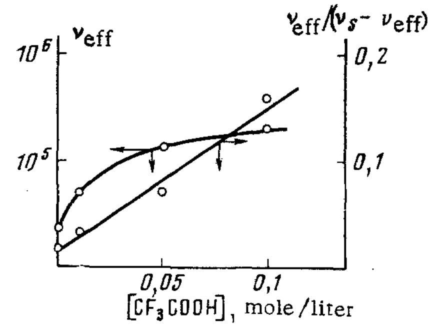


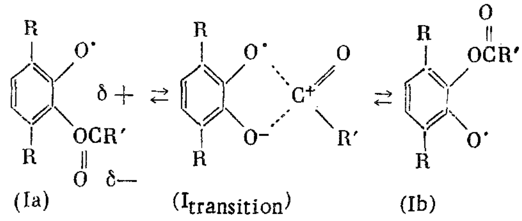
Fig. 2. Frequency of acylotropy in 3,6-di-tert-butyl-2-acetoxyphenoxyl as a function of the CF_3COOH concentration and its anamorphosis.

TABLE 2. Effect of Nature of Solvent on Kinetic Parameters of Acylotropy in 3,6-Di-tert-butyl-2-acetoxyphenoxyl

Solvent	$\nu(20°)$, sec^{-1}	ν_0, sec^{-1}	E_{act} ± 1.0 kcal/mole
$C_6H_5CH_3$	10^4	$0{,}9 \cdot 10^{13}$	11.4
C_6F_6	10^4	$9{,}1 \cdot 10^{13}$	13,5
CH_3NO_2	$4{,}4 \cdot 10^4$	$6{,}2 \cdot 10^{12}$	11,0
$C_6H_5NO_2$	10^5	$6 \cdot 10^{11}$	9,15
CH_3COOH	$1{,}4 \cdot 10^5$	$4 \cdot 10^{11}$	8,7
CF_3COOH (1 mole/liter in toluene)	$2{,}3 \cdot 10^6$	$6{,}7 \cdot 10^9$	4,7

where γ_e is the electron gyromagnetic ratio, and $\Delta(1/T_2)$ is the contribution to the line width due to exchange. The kinetic parameters of the acylotropic transitions for some of the studied radicals are given in Table 1. It can be seen that the acylotropy frequencies increase with increase in the acceptor properties of the substituents in the acyl group, while the energy barriers decrease. Besides this, the effect of the mass of the acyl group is not excluded, and here the frequency decreases with increase in the mass (cf. the acylotropy frequencies for the phenylacetyl and diphenylacetyl derivatives). These data make it possible to assume that the ease of migration of the acyl group with increase in the acceptor properties of the substituents is determined by the electron deficiency that is created on the carbonyl carbon atom, which facilitates the formation of a transition state of the ionic type (Itransition), via which the migration of the acyl groups is apparently realized.

A certain increase in the migration frequency with increase in the polarity of the medium (Table 2), and the positive acid catalysis of the acylotropy that was detected on the example of radical (I), testify in support of this interpretation of the acylotropy mechanism. In the presence of CF_3COOH the energy barrier drops in half, while the $\nu_{exchange}$ increases more than 100 times, in which connection the acylotropy frequency is accelerated with in-



crease in the acid concentration (Fig. 2). An electron deficiency on the carbonyl carbon atom is achieved via protonization of the C=O group in the acid—radical complex.

An analysis of the concentration and temperature functions of the acylotropy frequency in the presence of CF_3COOH made it possible to estimate the thermodynamic parameters of the complexing of radical (I) with the acid. The expression, relating the frequency in the free and solvated radicals (respectively ν_0 and ν_S) to the complexing constant (K_S), has the form

$$\nu_{\mathrm{eff}} = \frac{\nu_0 + \nu_s K_s[S]}{1 + K_s[S]}$$

where [S] is the CF_3COOH concentration, and ν_{eff} is the experimentally found acylotropy frequency. Taking into account that $\nu_0 << \nu_S$, it is possible to write

$$\nu_{\mathrm{eff}} = \frac{\nu_s K_s[S]}{1 + K_s[S]} \quad \text{or} \quad K_s[S] = \frac{\nu_{\mathrm{eff}}}{\nu_s - \nu_{\mathrm{eff}}}$$

Having plotted the anamorphosis of $\nu_{\mathrm{eff}}/(\nu_S - \nu_{\mathrm{eff}})$ vs the acid concentration [S], it is possible to estimate K_S. In Fig. 2 are plotted the function ν_{eff} vs the acid concentration and its anamorphosis. Having estimated K_S at various temperatures, we calculated the thermodynamic parameters of the complexing: $-\Delta H = 2.5$ kcal/mole, and $-\Delta S = 8$ entropy units.

EXPERIMENTAL

The studied radicals were obtained by the oxidation of the starting phenols in evacuated ampules using PbO_2 in toluene solution. The EPR spectra were recorded on a Varian E-12A spectrometer. The starting 3,6-di-tert-butyl-2-acyloxyphenols were obtained and characterized in [3].

CONCLUSIONS

1. The insertion of acceptor substituents into the acyl group increases the frequency of acylotropy in the corresponding radicals.

2. The positive acid catalysis of acylotropy was observed. The found effects of the substituents and acids are explained by the creation of an electron deficiency on the carbonyl carbon atom.

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