ESR ANALYSIS OF PROTON TRANSFER IN VISCOUS MEDIA

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The effect of the viscosity of a toluene solution, with addition of Vaseline oil, on the kinetics of proton transfer from 3,6-di-tert-butyl-2-hydroxyphenoxyl to triethylamine was analyzed by the ESR technique. Activation barriers of the reaction do not correlate with the viscosity's activation energy in these systems. The effects studied were attributed to van der Waals solvation of partners by long molecules of the Vaseline oil alkanes.

Keywords: proton transfer, 3,6-di-tert-butyl-2-hydroxyphenoxyl, activation parameters, ion pairs, viscosity.

The reverse reaction of proton transfer from 3,6-di-*tert*-butyl-2-hydroxyphenoxyl (1) to a tertiary amine, and with consideration given to hydrogen affinity [the degenerate tautomerism of the semiquinone radical (SR)], can be represented by the following genera scheme [1, 2]:



where S is the molecule of a solvating solvent.

In (1) both reaction channels are equivalent as the tautomeric forms A and A' are structurally indistinguishable. In indifferent, nonpolar solvents, the final stage of the reversible reaction of proton transfer is the formation of closed ion pairs of C and C' types. In the ESR spectrum, the triplet, with the CHFI at 0.335 mT, of an unpaired electron with two magneto-equivalent, ring protons corresponds to these pairs. The equivalence of the protons is based, in turn, on the quick $C \rightleftharpoons C'$ cation attraction in the ion pair of the semiquinone anion-radical with an ammonium cation. One should also take into consideration that the loosening of ion pairs by solvent molecules, for instance by those of tributylphosphate, prompts proton exchange between the A and D particles (A' and D') [2, 3]. On the other hand, while the A, C and (A', C') particles can be identified using ESR spectra (for they have different hfs and g factors), it proved impossible to record a separate ESR spectrum of the complex on the basis of the hydrogen bonds of the semiquinone radical 1 with triethylamine, because of the short life span of such bonds ($\tau_{BB'} < 10^{-9}$ sec).

A thorough spectral identification of the $A \rightleftharpoons B$ ($A' \rightleftharpoons B'$) equilibrium was attempted for the 1 — tributylphosphate (TBP) – Vaseline oil (VO) system. It was assumed that, because of the rate of the reverse reaction is low in the viscous medium of refined VO, it would be possible to record superposition of individual ESR spectra for the A and B (A' and B') particles, and that their g factors and HFI constants would be different. As can be seen from Fig. 1, over a wide temperature range the system is represented by an averaged ESR spectrum caused by quick ($\Delta \nu > 10^8 \text{ sec}^{-1}$) interchange of A and B particles (A' $\rightleftharpoons B'$).

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Fig. 1. Dynamic ESR spectra of the SP 1 – TBP-VO system at different temperatures (K): a) 293; b) 323; c) 373.

Fig. 2. Viscosity of the toluene-VO mixtures as a function of compositions at the following temperatures (K): a) 293; b) 303; c) 313; d) 323; e) 333; f) 343; g) 353; h) 363.

In the present study, the effect of the medium's viscosity on kinetics of the reverse proton-transfer reaction (1) was investigated, using the ESR spectrum method. For that purpose a number of toluene – refined VO mixtures were prepared, and the viscosities of the mixtures were measured at different temperatures. The dynamic viscosity of VO solutions in toluene is presented as a function of VO volume fractions at different temperatures by the curves in Fig. 2.

The ESR spectrum for SP 1 represents a triplet of doublets with the CHFI of an unpaired electron with a ring- and a hydroxyl-proton, equal, respectively, to 0.392 and 0.162 mT. As can be seen from Fig. 3, at low temperatures Eq. (1) shifts toward formation of the C and C' pairs, so that at -40° C, in the ESR spectrum, their corresponding triplet appears, with $a_{\rm H} = 0.335$ mT [3]. It follows from Fig. 3 that the ultimate right-hand-side hfs component of the ESR spectrum for 1 has the most pronounced width alternations of all the lines. The broadening $\Delta(1/T_2)$ of hfs lines is connected with kinetic parameters of reaction (1) by the following known expression [3, 4]:

$$\Delta (1/T_2) = \frac{\gamma_e \alpha (1-\alpha) (\Delta a)^2}{k_{-1}+k_1 [\text{ TEA }]}, \qquad (2)$$

where γ_e is the gyromagnetic ratio for the electron, $k_1 = k_{AC} + k_{A'C'}$, and $k_{-1} = k_{CA} + k_{C'A'}$ are specific rates of the direct and reverse reactions, Δa is the distance between hfs lines of the ESR spectrum for 1, broadened due to the exchange and presented in magnetic units, and α and $(1 - \alpha)$ are the magnetic parts of the A(A') and C(C') particles.

The $A \rightleftharpoons C$, $A' \rightleftharpoons C'$ equilibrium constant can be calculated from the following formula [3]:

$$K = \frac{a_0 - \tilde{a}}{\tilde{a} [\text{TEA}]}, \qquad (3)$$



Fig. 3. ESR spectra for the SP 1-TEA system in the toluene – VO mixture (9.5:0.5) at the following temperatures (K): a) 294; b) 274; c) 251.

Fig. 4. Logarithmic function $\log k$ vs $\log T/\eta$ at 293 K (η , cP): 1) reaction of proton transfer from SP 1 to TEA; 2) diffusion-controlled reaction in the toluene – VO mixture.

where \tilde{a} is the effective value of the hydroxyl splitting in the ESR spectrum of the 1-TEA-toluene-VO system, while a_0 is the same value in the absence of triethylamine (TEA).

The proof that the dynamic ESR spectra presented in Fig. 3 reflect kinetics of the bimolecular, reverse reaction A = C(A' = C') and not of B = C(B' = C'), i.e., proton transition inside the complex thanks to the hydrogen bond, lies in the fact that both the rate of process (1) and the size of the hydroxyl splitting in the ESR spectrum of 1 are linear functions of the triethylamine concentration [5]. This makes it necessary to evaluate the effect of diffusion properties of the medium on kinetics of this fast reaction of proton transfer.

The maximum reaction rate, controlled by translational diffusion k_D can be calculated from experimental values of the dynamic viscosity of the medium (η) , using the Debye formula [6, 7]:

$$k_{\rm D} = \frac{8RT}{3000\eta} \,. \tag{4}$$

Figure 4 presents that value as a logarithmic function of the medium's viscosity. It also presents, as a similar function, the rate constant of the proton transfer from 1 to triethylamine in a medium with suitable viscosity, evaluated by analysis of the width alternation of hfs lines of the ESR spectrum of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl. It can be seen from the graph that the rate of amine protonation by the radical does not exceed the diffusion limit, but approaches it as the viscosity of the medium increases.

Comparison of the activation parameters of reaction (1) with the medium's viscosity gave an ambiguous picture, presented in Fig. 5. While the viscosity's activation energy increases gradually with increase of the VO volume fraction, the activation barrier of the direct $\mathbf{A} \rightleftharpoons \mathbf{C}$ ($\mathbf{A} \rightleftharpoons \mathbf{C}'$) reaction has passes through a definite maximum at $E_1 = 56$ kJ/mole in low-viscosity solutions. It is a known fact that Vaseline oil represents a mixture of alkanes C_nH_{2n+2} (n = 10-16) [8]. It follows from Fig. 5 that the addition of VO to the 1-TEA-toluene system hinders the protonation reaction, whose rate is decreased with increasing viscosity of the medium. At high VO concentrations in the mixture, the activation barrier of the reaction changes in agreement with the medium viscosity's activation energy. As there is no specific solvation in refined VO, one can assume that small additions of an alkane mixture (VO) bond reaction partners through van der Waals interactions. To break such formations, apparently additional energy is required which increases the activation barrier. The decrease of activation



Fig. 5. Activation parameters as functions of the mixture's composition: 1) reaction of proton transfer from SP 1 to TEA; 2) diffusion-controlled reaction.

Fig. 6. ESR spectra for ionic pairs SP 1 with the trimethylammonium cation at the following temperatures (K): a) 231; b) 273 (VO as solvent).

barrier in response to large VO additions into an acid-alkaline system can probably be explained by the fact that intermolecular interaction between the VO's alkanes is stronger than between them and the reagents.

Slowing down of individual stages of the reaction (1) in the VO medium provides an opportunity to register spectra corresponding to slow exchange for the process of loosening of the closed ionic pair C(C') by excess molecules of a proton-acceptor, for instance triethylamine. Figure 6 presents superposition of ESR spectra for the C(C') and D(D') particles. Taking into consideration that loosening of closed ion pairs is an endothermic process, one can draw the conclusion that the pairs divided by he solvent have an ESR spectrum in the form of a triplet with $a_{\rm H} = 0.340$ mT shifted into a stronger field. The known decrease of g factors of anion-radicals was previously observed for the loosening of their ionic pairs with cations of alkali metals [9]. As can be seen from the ESR spectra, as the temperature decreases the amount of closed ion pairs in the systems increases.

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