compound. Redox reactions and ligand exchange can occur in principle. Based on the available data one cannot establish the nature of these reactions; one can only assume that these reactions are retarded on the basis of the slow increase in $S_1$.

Single radical particles are also formed at the potentials of the third wave. This is indicated by the increase in the intensity of $S_1$ of the single-radical signal (Fig. 3). Apparently, as in the case of the potentials of the second wave, chemical reactions take place between the products of three-electron reduction and the original molecule of the complex.

Let us point out in conclusion that the steep slopes, obtained in the reduction of nitroxy radicals in the protonated ligand LH in the complex ZnL$_2$ are apparently due to the influence of the preceding the subsequent protonation reactions on the reduction potential and to the insufficient mobility of the corresponding equilibria.

**LITERATURE CITED**


**EPR STUDY OF PROTONATION OF SUBSTITUTED THREE-MEMBER NITROGEN HETEROCYCLES**


The kinetics of fast proton transfer from 4-triphenylmethyl-6-tert-butyl-3-chloro-2-hydroxyphenoxyl to some three-member nitrogen heterocycles (1,2-dimethylaziridine, 1,2,3-trimethylidiaziridine, and 2-methoxymethyl-3-methyl-3-ethylhydroxyaziridine) were investigated by EPR and their kinetic basicity was estimated in comparison to proton acceptors with known $pK$. A comparison of the thermodynamic parameters of protolysis of the radical used in toluene solutions of the three-member heterocycles studied and known bases allowed estimating the $pK$ of these heterocycles (7-5).

The stable semiquinone radicals (SR), 3,6-di-tert-butyl-2-hydroxyphenoxyl (I) and 4-phenyl-6-tert-butyl-3-chloro-2-hydroxyphenoxyl (II), were previously used as paramagnetic probes for the EPR estimation of the kinetic basicity of different proton acceptors in a medium of organic solvents [1]. In the present study, this method was used for determining the rate of protonation of some strained heterocycles of 1,2-dimethylaziridine (DMA), 1,2,3-
trimethylidiaziridine (TMDA), and 2-methoxymethyl-3-methyl-3-ethylhydroxyaziridine (MEHA) to compare their proton-acceptor capacity with existing bases.

The EPR spectra of toluene solutions of semiquinone radical (I) with different DMA additives (pKₐ ~ 8.0) are shown in Fig. 1 [2]. The EPR spectrum of (I) is a triplet of doublets with HFI constants with ring and hydroxyl protons of 0.392 and 0.162 mT, respectively [1]. The disappearance of hydroxyl splitting in the EPR spectrum of (I) indicates protolysis of the radical in pure DMA medium (Fig. 1c). This process can be represented by Scheme (1) in consideration of the tautomerism in SR, which consists of intramolecular migration of a hydrogen atom between the oxygen atoms in the SR.

There is no hfs characteristic of contact ion pairs of the C,C' type in the EPR spectra of the SR-DMA-toluene system in wide variation of the concentration of proton acceptor and the temperature. This indicates that the basicity of DMA is lower than for thebaine (pKₐ = 7.0), for which a picture of "fast" reversible proton transfer is observed in similar conditions [1, 3]. The changes in the EPR spectrum typical of intramolecular proton exchange (Fig. 1b) are due to such a process between (I) and the conjugated acid: a loose ion pair of the semiquinone radical anion with the aziridinium cation. The endothermic character of disintegration of ion pairs causes the weak temperature dependence of the hfs in the EPR spectrum of the (I)-DMA-toluene system [1]. "Slow" proton transfer (ν < 10⁶ sec⁻¹) also takes place in the (I)-TMDA-toluene system, as seen from the superposition of the EPR spectra of (I) and the radical anion (Fig. 1d).

\[
\begin{align*}
\text{R} & \quad \text{OH} \quad \text{R}^1 \\
\text{R} & \quad \text{OH} \quad \text{R}^1 \\
\text{R} & \quad \text{OH} \quad \text{R}^1 \\
\text{R} & \quad \text{OH} \quad \text{R}^1 \\
\text{R} & \quad \text{OH} \quad \text{R}^1 \\
\text{R} & \quad \text{OH} \quad \text{R}^1 \\
\text{R} & \quad \text{OH} \quad \text{R}^1 \\
\text{R} & \quad \text{OH} \quad \text{R}^1 \\
\end{align*}
\]

S: molecule of solvent or excess proton acceptor.