KINETICS OF THE DEPROTONATION OF THE CATION-RADICALS FORMED IN THE ELECTROOXIDATION OF 1,2-DIHYDROPYRIDINES

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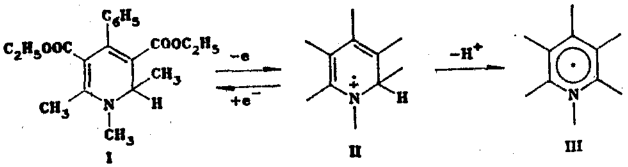
Using a rotating ring-disk electrode and EPR, it has previously been shown [1] that the initial product in the electrochemical oxidation of the 1,2-dihydropyridine (I) in acetonitrile is the relatively stable cation-radical (II), which in all probability is converted by deprotonation into the radicals (III), which are of low stability.



In order to establish the order and rate constant of the deprotonation of the cation-radicals (II), the rotating ring-disk electrode method was used to record the voltammetric plots at different angular velocities ω of the rotating electrode over a range of temperatures of the solvent used from 40° to −40°C. If the electrooxidation of (I) occurring at the disk electrode is a stationary process at the limiting current potential, then as Q is increased the number of molecules of (II) reaching the ring electrode should increase. The theoretical reaction for the disappearance of the intermediate product as a result of the occurrence of a first order homogeneous reaction is described by a straight line in coordinates Q, ω^{-1} [2]. Our experimental data confirm this behavior over the whole range of temperatures studied and concentrations of (I) from 5.10^{-4} to 5.10^{-3} mole/liter, confirming that the cation-radicals disappear as a result of deprotonation in solution.

A literature method [2, 3] was used to calculate the values of the rate constant for the deprotonation k, the half-life $\tau_{1/2}$, and the activation energy E_a for the cation-radicals (II) in acetonitrile: 40°C, $k = 11$ (±0.5) $\sec^{-1}$, $\tau_{1/2} = 0.06$ (±0.01) sec; and at −40°C $k = 2$ (±0.5) $\sec^{-1}$, $\tau_{1/2} = 0.35$ (0.01) sec, $E_a = 12$ kJ/mole. The half-life, calculated from cyclic voltammetry data under identical conditions, was 4 and 5 times as great respectively. Consequently, the deprotonation of the cation-radicals (II) proceeds more slowly on the electrode surface than in the bulk of the solution. The presence of a substituent at nitrogen and in the 4-position, and the addition of up to 5 mole/liter of water to the solution, had no effect on the values of the kinetic constants.

It is noteworthy that the cation-radicals formed during the electrooxidation of the corresponding isomeric 1,4-dihydropyridines are several orders of magnitude less stable, as a result of which the ring-rotating disk electrode and EPR cannot be used for their detection [4].

The measurements were carried out in acetonitrile (containing up to 5 mole/liter of water) with tetrabutylammonium perchlorate as the base electrolyte (0.1 mole/liter), at an electrode with a graphite disk and a platinum ring [5].

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