CATION RADICALS IN THE ELECTROCHEMICAL OXIDATION OF 2,6-DIMETHYL-3,5-ETHOXYCARBONYL-1,2-DIHYDROPYRIDINES

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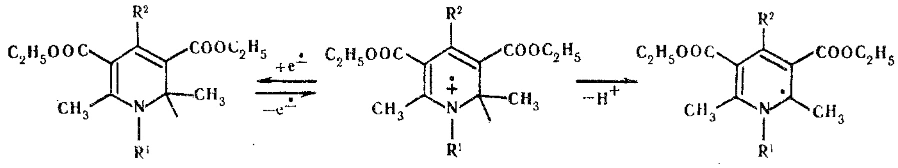
We detected quite stable cation radicals in the electrochemical oxidation of 1,4-disubstituted 2,6-dimethyl-3,5-bis(ethoxycarbonyl)-1,2-dihydropyridines (I) in acetonitrile. In a study of the electrochemical process on a rotating platinum disk electrode with a ring [1] in a thermostated electrolyzer at temperatures from +20 to −40°C and potentials ranging from 0.75 to 0.95 V we recorded a one-electron electrochemical oxidation wave on the disk and a wave of electrochemical reduction of the oxidation product on the ring electrode at the potentials of the foot of the oxidation peak (an anode-cathode wave). If the process is carried out by the method in [2] in an electrolyzer placed in the resonator of the EPR spectrometer [ER-9, Karl Zeiss (Jena)], at low temperature and potentials of the plateau of the limiting current of the one-electron wave one can record EPR spectra, in the hfs of which splitting by the nitrogen atom and the proton in the 2 position of the heteroring is displayed in all cases. For example, in the case of electrochemical oxidation of I ($R^1 = CH_3$, $R^2 = C_6H_5$) at −35°C the hfs of the EPR spectrum of the radical obtained is due to coupling of the unpaired electron with the lone proton in the 2 position of dihydropyridine ($a_N = 2.42$ G) and with the nucleus of the nitrogen atom ($a_H = 5.0$ G) and, in addition, to coupling with the protons of the methyl group attached to the nitrogen atom ($a_{H,NCH_3} = 5.0$ G).

The existence of a wave of electrical reduction of the proton on the ring also indicates the formation of radical III, although this radical could not be recorded by means of a rotating disk electrode with a ring. The manifestation of splitting by a long proton in the EPR spectrum constitutes evidence that the free radicals detected by EPR spectroscopy do not have the structure of pyridinyl radical III but rather are cation radicals II of starting I:



I II III

Cation radicals II were not recorded by EPR spectroscopy at room temperature. We also have not yet detected such cation radicals under the described conditions for the analogous 1,4-dihydropyridine derivatives with ethoxycarbonyl groups in the 3 and 5 positions.

LITERATURE CITED

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