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TWO POSSIBLE MECHANISMS FOR THE ELECTROCHEMICAL OXIDATION OF 1,2-DIHYDROPYRIDINES

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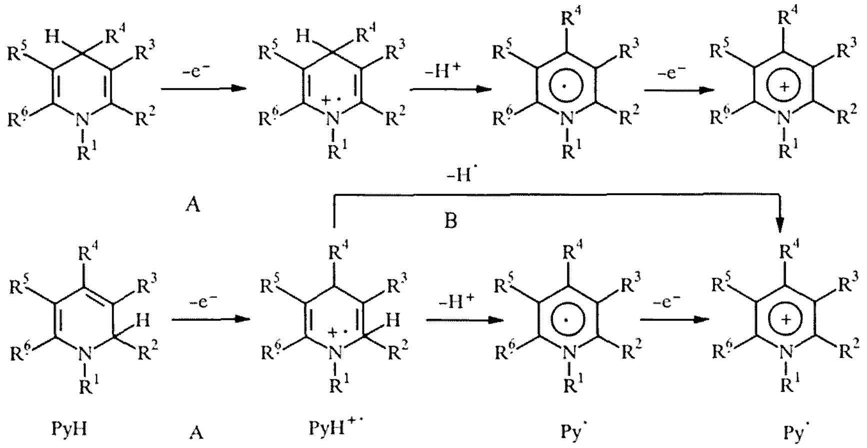
Three possible variants have been proposed to explain the mechanism of two-electron oxidation of derivatives of 1,4-dihydropyridines in chemical and photochemical reactions: a) a one step hydride transfer mechanism (H^- elimination); b) a two stage mechanism (e^-, $H^\cdot$ or $H^\cdot$, e^-); and c) a three step mechanism (e^-, H^+, e^-; or e^-, e^-, H^+; or H^+, e^-, e^-) [1-5].

The electrochemical oxidation of N-substituted 1,4-dihydropyridines and 1,2-dihydropyridines has been discussed on the basis of the third mechanism (more precisely its first variant), the removal of an electron to give a more or less stable cation–radical, which is then oxidized to the corresponding pyridinium salt by subsequent loss of a proton and an electron [6, 7]. Differentiation between mechanisms A and B (see Scheme) has been carried out by voltammetry at a rotating disk with a ring (VRDR), at least in the case of 2,6-dimethyl-3,5-dialkoxycarbonyl derivatives of 1,2-dihydropyridine.



$R^1 = CH_3$; C_6H_5; p-$CH_3C_6H_4$; p-$OCH_3C_6H_4$; $R^4 = C_6H_5$; p-$CH_3C_6H_4$; p-$OCH_3C_6H_4$;
$R^2 = R^6 = CH_3$; $R^3 = R^5 = COOC_2H_5$

It was concluded from examination of actual voltammetric curves at the disk and ring electrodes coupled with the theory of VRDR (an electro-oxidation reaction in which the product is rapidly quenched via a first order homogeneous chemical reaction) at different temperatures from +20 to −30°C that a cation radical is formed at some stage in all electro-oxidations of 3,5-dialkoxycarbonyl-1,4- and 1,2-dihydropyridines. At room temperature the cation-radicals predominantly underwent deprotonation to $Py^\cdot$ with subsequent oxidation, while at lower temperatures (i.e., with increased stability of the cation–radicals) oxidation by loss of $H^\cdot$ without formation of $Py^\cdot$ predominated. This rule was established experimentally for the substituted 1,2-dihydropyridines, whereas the most cation– radicals from the 1,4-dihydropyridines we studied were too unstable for their life times to be measured by the VRDR method. It appears that their electro-oxidation occurs only via deprotonation of the cation-radical and loss of an electron. The experimentally determined life times of the of the initially formed cation-radicals of the 1,2-dihydropyridines correlate linearly with the fraction of particles oxidized by route B. For

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example, for the 1,2-dihydropyridines (R^1 = CH_3, R^4 = *p*-$CH_3OC_6H_4$) at 20°C, 75% of the cation–radicals are deprotonated to give $Py^{\cdot}$ while the remaining 25% are converted to the final product Py^+ without loss of a second electron, i.e., by loss of $H^{\cdot}$. At −30°C only 35% of the same PyH^+ is deprotonated, the remaining 65% are converted to Py^+ by direct chemical reaction. In all cases the quantity of Py^+ formed corresponded to the amount of PyH which was oxidized electrochemically.

The electrochemical methodology and the general form of typical kinetic curves used in the calculations have been given elsewhere [8].

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