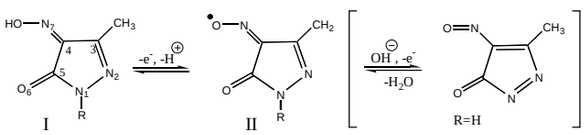
EXPERIMENTAL AND THEORETICAL STUDY OF ELECTROCHEMICAL OXIDATION OF 4-HYDROXYIMINOPYRAZOL-2-IN-5-ONES

V.V.Yanilkin[1], A.V.Toropchina[1], V.I.Morozov[1], G.A.Chmutova[2]

[1]A.E.Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences, Arbuzov str.8, 420088 Kazan, Russia. Fax: 7 (8432) 752253. E-mail: yan@iopc.knc.ru

[2]Kazan State University

The electrochemical oxidation of 1-R-3-methyl-4-hydroxyiminopyrazol-2-in-5-ones (I a-d) on glass carbon and platinum electrodes in acetonitrile has been studied by cyclic voltammetry and electrolysis in combination with ESR, *ab initio* RHF, ROHF and UHF (bases 6-31 G* - 6-311++G**) as well as by B3LYP method.



I, II (R = H (a), C_6H_5 (b), 4-BrC_6H_4 (c), 2-NO_2-4-$CF_3C_6H_3$ (d))

One-electron electrochemical oxidation results in formation of iminoxyl radicals in Z-configuration (II), oxidation potentials being significantly reduced with the increase of the basicity of the introduced bases (table). The radical of compound (I) in basic medium is further oxidized to 3-methyl-4-nitroso-pyrazol-1-in-5-one.

Experimental values of hyperfine coupling constants (g 2.0045, a_{N7} 30.78-31.33, a_{N1} 1.87-2.12) are reproduced by *ab initio* calculation only if electron correlation is taken into account (UB3LYP/6-31G*//UB3LYP/6-31G*). Calculated and analyzed were total energies of neutral molecules, cation and anion radicals and other particles, which arise or may arise while electrochemical oxidation in various conditions. The energy of distinct processes was studied depending on the tautomerism of initial compounds, substituents R, conformational and configurational effects etc.

Table. Oxidation potentials of compounds Ia-Id in MeCN/0.1 M Et_4NClO_4 and in the presence of bases at glasscarbon and Pt[a] electrodes

	E, V vs.Ag/0.01 M $AgNO_3$			
		+ Py	+ Pip	+TEAH
Ia	1.55	0.63	0.24	0.24
Ia[a]	1.96	0.83	0.23	0.24
Ib	1.16	0.64	0.30	0.27
Ib[a]	1.32	0.87	0.32	0.27
Ic	1.19	0.70	0.53	0.32
Ic[a]	1.44	0.68	0.51	0.29
Id	1.87	0.64	0.40	0.47
Id[a]	2.15	0.63	0.39	0.46

Py – Pyridine, Pip – Piperidine, TEAH - Et_4NOH