QUANTUM-CHEMICAL ESTIMATION OF OXYMETHYL RADICAL ACIDITY

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Kinetic and thermodynamic acidities of hydroxyl-containing free radicals are much higher than those of their diamagnetic analogs as was shown by numerous ESR spectroscopic studies. For example, according to the literature [1], the acidity of the oxymethyl radical $\cdot CH_2OH$ (pK_a=10.7) is higher than that of methanol (pK_a=15.5). The purpose of this study was a quantum chemical estimation of the oxymethyl radical pK_a value and its comparison with ESR-spectroscopic data.

Previously, it was shown [2-3] that deprotonation energy $\Delta E_{deprot.}$ can be used for quantum-chemical estimation of pK_a. Deprotonation energy ΔE_{deprot} can be estimated as the difference between total energies of the acid molecular form HA and its deprotonated residue A^-. The deprotonation energy of oxymethyl radical and some of its diamagnetic analogs was estimated by ab initio 6-31G UHF calculations with the help of Gaussian 2009 program:

№	Acid HA	E_{total} (HA), A.U.	E_{total} (A^-), A.U.	$\Delta E_{deprot.}$, A.U.	pK_a
1	HCOOH	-188,66548837	-188,09515411	0,5703343	3,75
2	CH_3COOH	-227,70111593	-227,12276412	0,5783518	4,76
3	$\cdot CH_2OH$	-114,36206719	-113,73957695	0,6224902	10,99(*)
4	CH_3OH	-114,98816535	-114,33863801	0,64952734	15,5
5	H_2O	-75,98535917	-75,31175325	0,6736059	15,7
6	C_2H_5OH	-154,01322917	-153,36795466	0,64527451	15,9

Equation of linear direct proportional relationship between deprotonation energy of diamagnetic objects and its pK_a value was obtained on the basis of the correlation analysis. This equation pK_a=132,11·$\Delta E_{deprot.}$-71,24 was used for quantitative assessment of oxymethyl radical pK_a(*) value. pK_a(*)=10.99 was obtained by substituting of the deprotonation energy value into linear correlation equation. Obtained pK_a(*) value is in a good agreement with the ESR-spectroscopic data.

References:

1. LAROFF, G.P., FESSENDEN, P.W. 1973 *J.Phys.Chem*., **77**, pp.1283-1295.
2. PUSTOLAIKINA, I.A. 2011. *Bulletin of the University of Karaganda-Chemistry*, **3** (63), pp.3-8.
3. PUSTOLAIKINA, I.A., VISURKHANOVA, Y.A., KUTZHANOVA, K.Zh. 2013. *Bulletin of the University of Karaganda-Chemistry*, **3** (71), pp.26-33.

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