COMPARING REACTIVITY OF PHTHALIMIDE-*N*-OXYL AND QUINOLINEIMIDE-*N*-OXYL RADICALS TOWARD THE C-H BONDS OF SUBSTITUTED BENZYL ALCOHOLS

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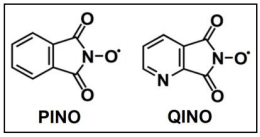

Benzyl alcohol and its substituted derivatives are model compounds for investigation of lignin oxidation process using laccase/*N*-OH mediator system. The activation of aliphatic C-H bonds with the participation of *N*-oxyl radicals is an important stage in the oxidation of benzyl alcohols in the presence of NOH-compounds. A comparative kinetic study of the reactivity of the quinolinimide *N*-oxyl radical (QINO) and the phthalimide *N*-oxyl radical (PINO) in the transfer of a hydrogen atom (HAT) with substituted benzyl alcohols was carried out. Radicals were generated by oxidation of *N*-hydroxyquinolinimide (NHQI) and *N*-hydroxyphthalimide (NHPI) with (diacetoxyiodo)benzene ($PhI(OAc)_2$) in acetonitrile.

Table. Second-order rate constants (k_H) for HAT from benzyl alcohol to QINO and PINO in CH_3CN at 303 K

p-X-$PhCH_2OH$	NHPI	NHQI
	k_H, $M^{-1}\times s^{-1}$	
MeO-	130	297
Me-	76	203
H-	29	79
Cl-	32	88
NO_2-	19	30

The kinetic studies QINO and PINO were performed by UV/Vis spectrophotometry in CH_3CN at 303 K. The UV/Vis spectra of the both radicals have similar view and presented a broad absorption band with λ_{max} is 382 nm. The buildup and decay of the *N*-oxyl radicals at this wavelength were recorded. The rate constants of H-abstraction (k_H) were calculated from the plots of pseudo-first-order rate constants *vs* substrate concentration. As seen in Table the HAT rate constants are significantly higher than those observed with PINO radical as a result of enthalpic and polar effects due to the presence of the *N*-heteroaromatic ring in QINO. A comparison of Hammett's correlations for the reactions of PINO (ρ = -0.55) and QINO (ρ = -0.66) with *p*-substituted benzyl alcohols is shown in the figure and indicates a similar reaction mechanism.

The results obtained show that NHQI is effective in reactions of the activation of C-H bonds and, along with NHPI, can be used in the catalytic aerobic oxidation of benzyl alcohols.

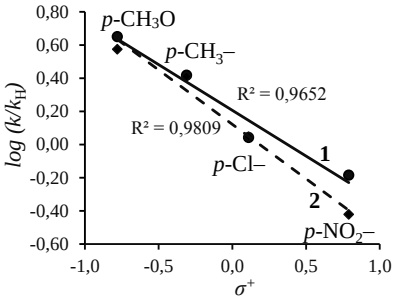

Fig. Hammett plot for the reactions of substituted benzyl alcohol with PINO (1) and QINO (2) in CH_3CN at 303 K ($[NHPIs]_0$ = 3.0 mM; $[PhI(OAc)_2]_0$ = 0.3 mM)