

**REACTIVITY OF PHTHALIMIDE N-OXYL RADICALS TOWARD  
THE C-H BOND OF BENZYL ALCOHOL**

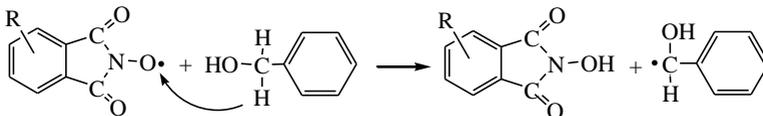
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Phthalimide-*N*-oxyl radical (PINO) is the important intermediate in the catalytic aerobic oxidation of benzyl alcohol to aldehyde. NHPI is oxidized by laccase to PINO and this reactive intermediate oxidizes non-phenolic lignin model compounds, such as benzyl alcohols, due to the ability to abstract hydrogen atom from the *α*-C-H bond. We investigated the kinetics of reaction of hydrogen atom transfer (HAT) from benzyl alcohol to the aryl substituted PINO with formation of initial NHPI and benzylic radical. This reaction is important in the catalyzed by NHPI aerobic oxidation of organic compounds.



The substituted *N*-hydroxyphthalimides such as 4,5-diCl-NHPI (1), 4-Cl-NHPI (2), 4-H-NHPI (3), 4-MeO-NHPI (4) were synthesized by reacting the corresponding phthalic anhydrides with hydroxylamine hydrochloride, using modified literature procedures. Radicals were generated by oxidation of the parent NHPI compounds with (diacetoxyiodo)benzene (PhI(OAc)<sub>2</sub>) in acetonitrile at 30 °C. The UV/Vis spectra of the aryl substituted PINO radicals present a broad absorption band with  $\lambda_{\text{max}}$  respectively 410 nm for (1), 401 nm (2), 382 nm (3) and 496 nm (4) in CH<sub>3</sub>CN. Pseudo-first-order rate constants ( $k_{\text{obs}}$ , c<sup>-1</sup>) of H-abstraction from benzyl alcohol by the aryl substituted with either electron-withdrawing (Cl-) or electron-donating groups (CH<sub>3</sub>O-) PINOs were determined. The rate constants of H-abstraction were calculated from the plots of  $k_{\text{obs}}$  on substrate concentrations (see Fig.). They are equal to 68.1 (1), 49.9 (2), 29.0 (3) and 15.8 (4) M<sup>-1</sup>s<sup>-1</sup>, accordingly.

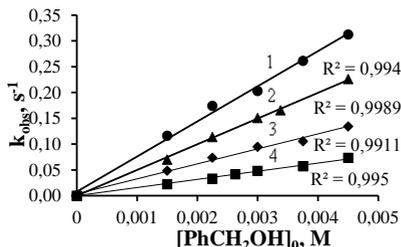


Fig. Plot of  $k_{\text{obs}}$  against concentration of benzyl alcohol: 4,5-diCl-PINO (1), 4-Cl-PINO (2), PINO (3) and 4-MeO-PINO (4); [NHPIs]<sub>0</sub> = 3.0 × 10<sup>-3</sup> M; [PhI(OAc)<sub>2</sub>]<sub>0</sub> = 3.0 × 10<sup>-4</sup> M, [PhCH<sub>2</sub>OH]<sub>0</sub> = 1.5 ÷ 4.5 × 10<sup>-3</sup> M

The reactivity of substituted PINO follows the order 4-MeO < 4-H < 4-Cl < 4,5-diCl, which corresponds to the order of the O-H bond dissociation energies (BDE) of the parent NHPI compounds. Alternatively, the acceleration of the rate constants by electron withdrawing groups might be explained by a polar effect at the transition state. It's confirmed by Hammett correlation for reaction of NHPI with *p*-substituted benzyl alcohols.

A Hammett correlation obtained on plotting log  $k_X/k_H$  vs.  $\sigma$  gave a  $\rho$  values of -0,56.