

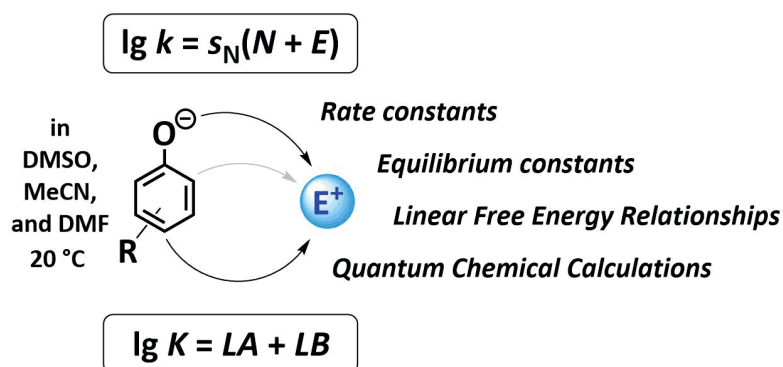
AMBIDENT REACTIVITY OF PHENOLATE ANIONS REVISITED: A QUANTITATIVE APPROACH TO PHENOLATE REACTIVITIES

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Phenolate ions are ambident nucleophiles, which may react with electrophiles either at oxygen or at carbon. Prompted by the observation that the regioselectivities of their reactions with electrophiles are exactly the opposite to the predictions by the HSAB principle,^[1] a comprehensive experimental and computational investigation of phenolate reactivities was performed. By studying rate and equilibrium constants for the reactions of phenolate ions with benzhydrylium ions and related quinone methides in various solvents, the nucleophilicity and Lewis basicity for oxygen-attack as well as the nucleophilicity of carbon attack could be determined. Thus, a series of phenolate ions could be integrated into established reactivity scales.^[2]



Except for diffusion limited reactions, O-attack of phenolates is strongly favored under kinetically controlled conditions whereas C-attack is strongly favored under thermodynamically controlled conditions. Product ratios are rationalized by a combination of kinetic and thermodynamic parameters of the phenolates and their electrophilic reaction partners. Furthermore, electrochemical data^[3] reveal that the reactions of phenolates with carbocations proceed via polar mechanisms.

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