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Effect Of Hybridization Of Carbon On Hammett Reaction Constant (ρ): π -Electron Transmission Versus σ -Electron Insulation: A Motivating Lecture For Graduate Students Of Physical-Organic Chemistry Class-Room

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ABSTRACT

The presence of sp² carbons in a side chain of benzene ring resulted in a significant increase in Hammett ρ value by a factor of two in the dissociation equilibriums of cinnamic acids (XC₆H₄CH=CHCOOH) and by a factor of five in the dissociation equilibriums of 5-phenylpenta-2,4-diecoic acids (cinnamylidene acetic acids; XC₆H₄CH=CH-CH=CHCOOH) compared to the dissociation equilibriums of phenyl propionic acids ($XC_6H_4CH_2CH_2COOH$) and 5-phenylpentanoic acids ($XC_6H_4CH_2CH_2CH_2COOH$) respectively. This concept is explained in a simple protocol based on the fact that σ bonds are localized. They form the covalent bonds between the carbon atoms. The π electrons in a conjugated double bond system are not relatively localized and not as strongly bound as the σ electrons. Only π -electron transmission through sp² carbons in cinnamic acids and 5-phenylpenta-2,4-diecoic acids is solely responsible for high values of Hammett ρ . And σ -electron insulation coupled with attenuation effect of two and four methylene groups in phenyl propionic acid and 5-phenylpentanoic acid dissociation equilibriums respectively ended with very low Hammett ρ values. This is undoubtedly an interesting lecture for graduate students of physical-organic chemistry class-room. The presence of sp carbons in the side chain has affected the Hammett's ρ value in the 5-phenylprop-2,4-diynoic acid (XC₆H₄C \equiv C-CCOOH) equilibriums even more effectively when compared to the dissociation equilibriums of 5-phenylpentanoic acids ($XC_6H_4CH_2CH_2CH_2CH_2COOH$) again.

Keywords: Attenuation effect, methylene group, acid dissociation equilibriums, π -electron transmission, σ -electron insulation.