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CONCERNING THE IMPORTANCE OF DUAL ρ_π CONCEPT IN THE LSFE TREATMENT FOR THE SUBSTITUENT EFFECTS ON BASICITIES OF PYRIDINES AND PYRIDINE N-OXIDES

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The relative dissociation constants of both meta and para substituted pyridinium ions in H_2O at 25°C were collected from a number of sources. To understand the actual substituent effects with a combination of inductive(I) and pi-electronic(Pi) effect components, the LSFE Eq. 1 has been employed statistically for each of meta and para series:

$$\log k/k_o = \rho_i\sigma_i + \rho_\pi^+\sigma_\pi^+ + \rho_\pi^-\sigma_\pi^- , \qquad (1)$$

where $\sigma_i = 0.74\sigma'$, $\sigma_\pi^+ = 0.415(\sigma^+ - \sigma^o)$, $\sigma_\pi^- = 0.73(\sigma^- - \sigma^o)$, and then, $\sigma_p^o = \sigma_i + \sigma_\pi^+ + \sigma_\pi^-$, $\sigma_p = \sigma_i + 1.65\sigma_\pi^+ + \sigma_\pi^-$, $\sigma_p^+ = \sigma_i + 3.41\sigma_\pi^+ + \sigma_\pi^-$, and $\sigma_m = 1.17\sigma_i + 0.50\sigma_\pi^+ + 0.50\sigma_\pi^-$ on benzene reactivities. The statistical application of Eq. 1 to the present pyridine sets afforded the following results.

$$(\Delta pK_a)_{para} = 6.40\sigma_i + 9.20\sigma_\pi^+ + 2.39\sigma_\pi^- - 0.03;$$

R= 0.9965, s= ±0.228, n= 15 (Me, Et, Cl, Br, MeO, NH_2, NMe_2, Ph, H, CF_3, COMe, CN, NO_2, COPh, COOMe).

$$(\Delta pK_a)_{meta} = 7.60\sigma_i + 3.02\sigma_\pi^+ + 2.25\sigma_\pi^- - 0.03;$$

R= 0.9973, s= ±0.149, n= 14 (Me, Et, F, Cl, Br, MeO, NH_2, NMe_2, H, COMe, CN, NO_2, COPh, COOMe).

The important features of the results are (i) the ratio of inductive component for meta to para substituents, $\rho_{i,meta}/\rho_{i,para}$, is 1.19, which is virtually identical with 1.17 in the corresponding benzene system, and (ii) in the Pi effect, the contribution of pi-acceptor substituents at para position (ρ_π^-) is very small relative to that of either ρ_π^+ or ρ_i, but definitely non-negligible: we note here that the apparent large ρ_π^+/ρ_π^- (ca. 4) does not mean a large resonance exaltation of pi-donor substituents classified as σ^+-type reactivity.

From these results, it is clear that the I effect in pyridine system is position-dependent, and the I effect from meta position is 1.2 times more effective than that from para one. By elimination of the I effect using its contribution factor of 0.85(=1/1.19), a pi-electronic effect equation should be constructed for the combined data set of meta and para substituents, without the use of any inductive parameters:

$$(\Delta pK_a)_{para} - 0.85(\Delta pK_a)_{meta} = 6.6\sigma_\pi^+ + 0.5\sigma_\pi^- .$$

This illustrates that in the Pi effect, there exists a bilinear relationship for pi-donor and pi-acceptor substituents bisected at the unsubstituted point, and there is not any other existing scales of single substituent constants with which this characteristically unbalanced Pi effect can be accounted for. Further, the substituent effects on basicities of pyridine N-oxides have been well treated in the similar manner.

Combined with earlier results by Taft's DSP and other relevant treatments, the soundness of the dual ρ_π approach and the superiority of the LSFE treatment have been demonstrated.