REEXAMINATION OF THE SUBSTITUENT EFFECTS FOR BASICITIES OF PYRIDINES AND QUINOLINES IN WATER

Masami Sawada, Masaharu Ichihara, Takashi Ando,
Yasuhide Yukawa, and Yuho Tsuno*

The Institute of Scientific and Industrial Research, Osaka Univ., Suita, Osaka 565
*Department of Chemistry, Faculty of Science, Kyushu Univ., Hakozaki, Fukuoka 812

The relative dissociation constants of meta and para substituted pyridinium ions in H_2O at 25^0C 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 equation has been employed statistically.

$$\text{para;}\quad \Delta pK = 6.40\,\sigma_i + 9.20\,\sigma_\pi^+ + 2.39\,\sigma_\pi^-$$

$$\text{meta;}\quad \Delta pK = 7.60\,\sigma_i + 3.02\,\sigma_\pi^+ + 2.25\,\sigma_\pi^-$$

From the excellent correlations obtained, it is clear that (i) the I effect from meta position is 1.2 times more effective than that from para one, the figure of which is identical with that in general benzene reactivities, (ii) the Pi effect in para position provides characteristically different sensitivities for pi-donor(-R) and pi-acceptor(+R) classes of substituents; that is, more exalted and more depressed Pi effects than that involved into σ^0 constants for -R and +R groups, respectively.

The LSFE equation has been also applied to the relative basicities of quinolines.

$$\text{3-substs;}\quad \Delta pK = 6.30\,\sigma_i + 1.41\,\sigma_\pi^+$$

$$\text{4-substs;}\quad \Delta pK = 5.34\,\sigma_i + 10.80\,\sigma_\pi^+$$

$$\text{5-substs;}\quad \Delta pK = 3.96\,\sigma_i + 3.45\,\sigma_\pi^+ + (1.18)\,\sigma_\pi^-$$

$$\text{6-substs;}\quad \Delta pK = 3.00\,\sigma_i + 2.23\,\sigma_\pi^+ + 2.37\,\sigma_\pi^-$$

$$\text{7-substs;}\quad \Delta pK = 3.63\,\sigma_i + 4.41\,\sigma_\pi^+ + 2.54\,\sigma_\pi^-$$

In this series, we found that there exist the positional constancies of I effects, $C_{ij}=\rho_i/\rho_{i,4}$, in the quinolinium system, which are equivalent to those from various 1-naphthyl reactivities, such as solvolysis of 1-(1-naphthyl)ethyl chlorides.

Compared with earlier results from Taft's DSP and relevant treatments, the soundness of the dual ρ_π approach, and further, the superiority of the LSFE treatment have been demonstrated. Furthermore, a new and complete set of σ^0 scales of pyridyl and quinolyl groups has been determined and then, the aza substituent effects have been discussed in the similar line.