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SUBSTITUENT EFFECTS IN THE PYRIDINE SYSTEMS

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Early rationalization of the substituent effects on the basicities of pyridines or pyridine N-oxides includes Jaffe's, Fischer's, and Taft's recognition of the use of various substituent parameters. However, since there are controvertial problems on such rationalization, a more quantitative and unified description at an advanced level have been waited. We find that the LArSR treatment which has potential advantages of describing the dual resonance effects for pi-donor(r^+) and pi-acceptor(r^-) substituents can provide a simple and strong power to solve the complicated problems.

$$P - P_o = \rho\ (\sigma^o + r^+\Delta\bar{\sigma}_R^+ + r^-\Delta\bar{\sigma}_R^-) \qquad (1)$$

The pyridine basicity set is characterized in terms of a weakly exalted resonance contribution from pi-donors(r^+=0.2) and uniquely a deminished resonance contribution from pi-acceptors(r^-=-0.5). On the other hand, the pyridine N-oxide basicity set gives a more exalted pi-donor resonance(r^+=0.6) and also an exalted pi-acceptor resonance contribution(r^-=0.2). The increases in the magnitude of r^+ and r^- on going from the pyridine to the pyridine N-oxide system is just consistent with those on going from σ^o to σ^- in the benzene system.

The quinuclidine basicity set classified into typical saturated reactivity is successfully described by means of the LArSR Eq(1) with r^+=-0.43 and r^-=-0.79. Importantly, any inductive substituent parameters from saturated systems are not employed in this treatment. Therefore, from these results, we can nicely determine the adequate amount of pi-donor and pi-acceptor resonance contributions and further, the inductive contribution involved into the σ^o constants in aromatic reactivities.

The rates of the reverse Menschutkin reaction of N-methylpyridinium iodides in the presence of triphenylphosphine were determined by means of ^{31}P-NMR quantitative measurements. The reactivity set provides the same r^- (=-0.5) as that in the pyridine basicity. Conclusively, the LArSR Eq(1) can describe the substituent effects in general pyridine reactivities most reasonably and, most conveniently, in the analogous way to those in general benzene reactivities.