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Relative σ Donor Ability of Pyridines, Imidazoles, and Pyrazoles

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The methylmercury(II) cation is a typical Class B cation or soft acid [1, 2], and as it usually binds to only one donor atom [2, 3] it is an ideal ion for investigating the donor properties of unidentate ligands. The coupling constant $^2J(^1H-^{199}Hg)$ is a useful spectroscopic probe in studies of $MeHg^{II}$ complexes MeHgX and [MeHgL]X, in particular $^2J(^1H-^{199}Hg)$ varies with the type of donor atom (*e.g.* N, O, S, Se) and varies linearly with the basicity of X^- or L [2], *e.g.* for complexes of substituted pyridines $^2J(^1H-^{199}Hg)$ decreases with both increasing log K_H (pKa of LH^+) [5, 6] and gas phase enthalpies for ionization of LH^+ [6]. We report here an application of ^1H NMR spectroscopy of $MeHg^{II}$ complexes to obtain an estimate of the relative σ donor abilities of closely related heterocyclic ligands towards soft acids.

Trends in $^2J(^1H-^{199}Hg)$ with variation of log K_H have been explained by assuming that the relative magnitude of the coupling constant is due mainly to the Fermi contact interaction, reflecting the s electron density on the coupled nuclei and carbon and the s character of the hybrid orbital on mercury bonding to carbon [7]. With bonding in linear [8] [MeHgL]X complexes considered to be essentially σ bonding, based on sp hybridization for mercury [9], the coupling constant will reflect the relative σ donor ability of ligands L towards $MeHg^{II}$ and presumably toward other soft acids. Stronger Hg–ligand bonding is expected to result in lower values for $^2J(^1H-^{199}Hg)$, *e.g.* for formation of MeHgCl from $MeHg^+$ and Cl^- log K = 5.25, ΔH = −6.0 kcal mol^{-1} [10], $^2J(^1H-^{199}Hg)$ = 215.2 Hz [11], and for MeHgBr log K = 6.62, ΔH = −9.9 kcal mol^{-1} [10], $^2J(^1H-^{199}Hg)$ = 212.0 Hz [11].

We have extended our previous studies of [MeHgL]X (L = substituted pyridines (py) [5, 6] and imidazoles (NRIm) [4]) to include the related substituted pyrazoles (NRPyz), and find that for all three types of ligand $^2J(^1H-^{199}Hg)$ decreases with increasing log K_H (Fig. 1), *i.e.* as the σ donor ability towards the hard acid H^+ increases so also does the donor ability of the ligands towards the soft acid $MeHg^{II}$. Consistent with this the complex [MeHg(NMeIm)]$^+$ has a higher stability constant (log K 6.96 [2]) than [MeHg(pyridine)]$^+$ (log K 4.8 [12], 4.72 [13]).

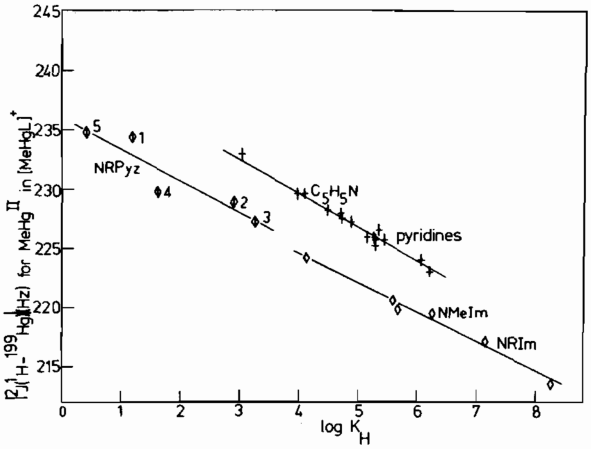
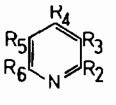
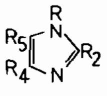


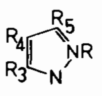
Fig. 1. $|^2J(^1H-^{199}Hg)|$ for $[MeHgL]NO_3$ (in CD_3OD) *vs.* log K_H for the ligands (L). Log K_H values are those obtained for a 50% dioxane-water mixture as solvent: (+) L = pyridines; (◇) substituted imidazoles; (◆) substituted pyrazoles. Values of $^2J(^1H-^{199}Hg)$ and log K_H for pyridine complexes, except for diphenyl-2-pyridylmethane (232.7 Hz, 3.04), and N-alkylimidazole complexes are given elsewhere [4–6]. The new complexes $[MeHgL]NO_3$ have $^2J(^1H-^{199}Hg)$ and log K_H of LH^+ as follows: (1) N-methylpyrazole (234.3 Hz, 1.19), (2) 3,5-dimethyl-N-methylpyrazole (228.8 Hz, 2.90), (3) 3,4,5-trimethyl-N-methylpyrazole (227.2 Hz, 3.26), (4) 3,5-dimethyl-N-phenylpyrazole (229.7 Hz, 1.62), and (5) N-benzyl-pyrazole (234.7 Hz, 0.42). The new complexes were prepared from acetone solutions of $MeHgNO_3$ and ligand, and have satisfactory microanalyses (C, H, Hg). For pyridine complexes $^2J(^1H-^{199}Hg)$ = −2.83 log K_H + 240.9 Hz (correl. coefft. −0.98 [6]), for substituted imidazole complexes $^2J(^1H-^{199}Hg)$ = −2.50 log K_H + 234.6 Hz (correl. coefft. −0.98 [4]), and for substituted pyrazoles $^2J(^1H-^{199}Hg)$ = −2.691 log K_H + 235.9 Hz (correl. coefft. −0.93).



py



NRIm



NRPyz

In addition the correlations for substituted imidazoles and pyrazoles are displaced from the correlation for pyridines towards *lower* $^2J(^1H-^{199}Hg)$ values. This suggests that *for ligands with similar protonation constant log K_H* the substituted imidazoles and pyrazoles are better σ donors than pyridines toward soft acids.

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