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Some ¹⁹⁹Hg–¹H Spin–Spin Coupling Constants

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There is a good correlation between the 199 Hg-1H coupling constants in RCO2HgMe compounds and the pK values of the acids RCO₂H. ¹⁹⁹Hg-¹H coupling constants in aryl-mercury derivatives parallel quite closely the corresponding ²⁰⁵TI-¹H and ¹H-¹H coupling constants.

THERE is evidence 1-4 that the magnitudes of heavymetal proton spin-spin coupling constants are largely determined by the Fermi contact interaction, although this has been questioned.⁵ Mercury has one isotope with spin $\frac{1}{2}$, ¹⁹⁹Hg, 16.9% abundant, and a number of ¹⁹⁹Hg--¹H coupling constants have been reported in the literature. In particular, Hatton, Schneider, and Siebrand ¹ have shown that the variation in $J(^{199}Hg-^{1}H)$

for complexes of the type MeHgX can be understood in terms of changes in the s character of the Hg-C bond, and the optical hyperfine structure constant of the mercury atom (the latter is approximately related to the effective nuclear charge of the mercury atom). On this basis, the greater the electronegativity of X, the larger will be the numerical value of $I(^{199}Hg-^{1}H)$, or, since ³ A. D. Cohen and K. A. McLauchlan, Mol. Phys., 1963, 7,

¹ J. V. Hatton, W. G. Schneider, and W. Siebrand, J. Chem. Phys., 1963, 39, 1330.
² J. P. Maher and D. F. Evans, J. Chem. Soc., 1965, 637.

^{11.} ⁴ G. D. Shier and R. S. Drago, J. Organometallic Chem., 1966, **5**, 330. ⁵ W. McFarlane, J. Chem. Soc., 1967, 725.

 $J(^{199}\text{Hg}^{-1}\text{H})$ almost certainly has a negative absolute sign,⁶ the smaller will be the absolute value of $J(^{199}\text{Hg}^{-1}\text{H})$. Since the electronegativity of a group X is often known only approximately, we have studied a series of methylmercury carboxylates RCO_2HgMe . In these, the immediate environment of the mercury atom is the same in all cases, and a measure of the effective electronegativity of the group RCO_2^- can be obtained from the pK of the acid RCO_2H . A number of aryl-mercury derivatives have also been studied, in order to compare the ¹⁹⁹Hg⁻¹H coupling constants with the corresponding ²⁰⁵Tl⁻¹H coupling constants previously reported.²

EXPERIMENTAL

 1 H n.m.r. were measured at 56.45 Mc./sec. on a Varian 4311 spectrometer. Analysis of the spectra was straightforward, although some splittings could not be detected because of the low abundance of the ¹⁹⁹Hg isotope.

The methylmercury carboxylates were prepared by shaking methylmercuric iodide in slight excess with an ethanol suspension of the appropriate silver salt for ca. 3 hr. The filtrate was evaporated to dryness, and the residue recrystallized from alcohol or benzene-light petroleum.

The aryl-mercury acetates were obtained either by direct mercuration of the hydrocarbon with mercuric acetate, or from the aryl-boronic acid and mercuric acetate.

4,7-Dimethyl-1-naphthylmercuric acetate.—4,7-dimethyl-1naphthylboronic acid (5 g.) in methanol (100 ml.) was refluxed for 5 min. with mercuric acetate (8 g.) in water (50 ml.) containing a trace of acetic acid. The mixture was cooled in ice, and the product recrystallized from chloroform. Yellow crystals, m.p. 168—170° (Found, C, 40.5; H, 3.35; O, 7.6. C₁₄H₁₄HgO₂ requires C, 40.5; H, 3.4; O, 7.7%).

RESULTS AND DISCUSSION

Methylmercury Carboxylates.—The 199 Hg–¹H coupling constants are given in Table 1, together with the pK

TABLE 1

¹⁹⁹Hg-¹H coupling constants (c./sec.) for RCO₂HgCH₃ compounds (10% solutions in alcohol-free chloroform), and the pK values of the acids RCO₂H

D	J(199Hg-1H)	\ T
ĸ	(c./sec. ± 0.5) pr
CH ₃	. 212.4	4·76 °
C.H	. 214.8	4·20 ª
p-NÖ ₂ C ₆ H ₄	. 216.2	3·44 ª
CH,CI	. 217.9	2·87 ª
CHĊl,	. 222.8	1·26 ª
CF ₃	. 228.4	-0·26 b
a B	lef. 7. ^b R	ef. 8.

values of the acids RCO_2H . It can be seen that there is a close correlation between these two properties (see Figure) which is consistent with the discussion above. That the plot of $J(^{199}\text{Hg}_{-1}\text{H})$ against pK is apparently a straight line, rather than a curve, is presumably due to the comparatively small range of the $^{199}\text{Hg}_{-1}\text{H}$ coupling constants. Aryl-mercury Derivatives.—The ¹⁹⁹Hg_-¹H coupling constants are presented in Table 2. They parallel quite closely the ²⁰⁵Tl-¹H coupling constants in the corresponding R_2Tl^+ and RTl^{2+} cations, which in turn are related to the analogous proton-proton coupling





constants.² The discussion given in the previous paper ² is thus directly applicable. A comparison can be made between corresponding ²⁰⁵Tl-¹H and ¹⁹⁹Hg-¹H coupling constants for the R_2Tl^{2+} and AcOHgR species in nine

TABLE 2

¹⁹⁹Hg-¹H coupling constants (c./sec.) for aryl-mercury derivatives. Solvent is CHCl₃ or CDCl₃ except for 2thienylmercuric chloride (dioxan)



cases. The ratio $J(^{205}\text{Tl}-^1\text{H})/J(^{199}\text{Hg}-^1\text{H})$ is not constant, but only varies from $4\cdot5-...7\cdot6$ (or $1\cdot4-...2\cdot4$ for the reduced coupling constants), while the nine $^{199}\text{Hg}-^1\text{H}$ coupling constants cover the range $7\cdot3-...202$ c./sec. The $^{199}\text{Hg}-^1\text{H}$ coupling constants in 3-chloromercurifuran have been measured by Cohen and McLauchlan ³ and are similarly closely related to the corresponding proton-proton coupling constants in furan itself.³

We thank the S.R.C. for a maintenance grant (to I. W.).

[7/1673 Received, December 21st, 1967]

⁷ G. C. Hood, O. Redlich, and C. A. Reilly, J. Chem. Phys., 1955, 23, 2229.

⁶ G. Kortüm, W. Vogel, and K. Andrussow, 'Dissociation Constants of Organic Acids in Aqueous Solution,' Butterworths, London, 1961.

⁸ K. A. McLauchlan, D. H. Whiffen, and L. W. Reeves, Mol. Phys., 1965, **10**, 131.