

MERCURY-PROTON SPIN-SPIN COUPLING CONSTANTS OF SOME METHYLMERCURY COMPOUNDS

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SUMMARY

The ^{199}Hg - ^1H spin-spin coupling constants for methylmercury salts of 36 organic acids, CH_3HgX (where $\text{X} = \text{OR}^-$, SR^- or OOCR^-), were determined. A linear relationship between the coupling constants and the pK 's of the monobasic parent acids was found. The magnitudes of the coupling constants are dependent on the type of basic site, decreasing in the order $\text{CH}_3\text{HgOR} > \text{CH}_3\text{HgOOCR} > \text{CH}_3\text{-HgSR}$, *i.e.*, with increasing covalent character of the HgX bond. The anomalous behavior of some dibasic acid salts is discussed.

The proton magnetic resonance spectra of methylmercury compounds are characterized by intense methyl group singlets at approximately τ 9 and two weak satellite peaks caused by coupling between ^{199}Hg nuclei (16.8% abundant, spin 1/2) and the methyl protons. Coupling constants previously reported for compounds of the types $\text{CH}_3\text{HgOOCR}^{1,2}$ and $\text{R}_2\text{Hg}^{3,4}$ show a linear relationship to the pK values of the corresponding acids HOOCR or HR . This is true because the magnitudes of the coupling constants and the pK 's are both related to the polarizabilities of the basic sites to which the methylmercury group and the proton are bonded. However, the J - pK relationship is not expected to hold if the base ion has more than one basic site because the bonding preferences of the proton (a hard acid) and the methylmercury cation (a soft acid) may differ⁵. It would seem possible, therefore, to use the coupling constants of methylmercury compounds and their relationship to the pK 's of the corresponding acids as an indication of the point of attachment of the methylmercury groups.

In this paper we report coupling constants for some methylmercury salts of carboxylic acids, phenols, and thiophenols to test more extensively the J - pK relationship for monobasic acids. We have also included some derivatives of acids in which a choice of basic sites is available and have drawn some structural inferences from the J - pK relationships we have found.

EXPERIMENTAL SECTION

The methylmercury salts were prepared by three different methods, labelled

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TABLE 1

PREPARATIONAL DATA FOR METHYLMERCURY COMPOUNDS

Parent Acid <i>RXH</i>	Method of preparation ^a	Recryst. solvent	Melting point (°C) ^c	Analysis found (calcd.)(%)		
				C	H	N
<i>A. X = O</i>						
Phenol	A	Hexane/methylene chloride	129(130)	27.10 (27.21)	2.62 (2.60)	
<i>p</i> -Chlorophenol	A	None ^b	125(dec.)	24.33 (24.51)	1.68 (2.05)	
1-Naphthol	A	Hexane/methylene chloride	91(dec.)	36.76 (36.80)	2.82 (2.80)	
<i>p</i> -Bromophenol	A	None ^b	130(dec.)	21.09 (21.67)	1.64 (1.81)	
<i>m</i> -Bromophenol	C	Hexane/methylene chloride	101	21.88 (21.67)	1.65 (1.81)	
<i>o</i> -Bromophenol	B	Hexane/methylene chloride	88	21.74 (21.67)	1.81 (1.81)	
2,4-Dichlorophenol	A	Hexane/methylene chloride	135	22.58 (22.24)	1.37 (1.59)	
8-Hydroxyquinoline	A	Hexane	99(90)	33.42 (33.36)	2.48 (2.52)	4.07 (3.89)
<i>p</i> -Formylphenol	A	None ^b	135(dec.)	28.25 (28.51)	2.24 (2.39)	
<i>p</i> -Nitrophenol	A	None ^b	167(dec.)	24.19 (23.82)	1.73 (1.99)	3.92 (3.96)
5-Acetyl-8-hydroxyquinoline	B	None ^b	163	36.14 (35.92)	2.65 (2.76)	3.65 (3.48)
Pentafluorophenol	B	Hexane/methylene chloride	134	20.98 (21.07)	0.98 (0.89)	
<i>B. X = S</i>						
Cyclohexylmercaptan	B	Water/acetone	65	25.61 (25.40)	4.16 (4.26)	
<i>p</i> - <i>t</i> -Butylthiophenol	B	Hexane	89	34.72 (34.67)	4.46 (4.23)	
<i>p</i> -Methylthiophenol	B	Hexane	75	28.95 (28.34)	2.81 (2.96)	
<i>o</i> -Methylthiophenol	B	Hexane	75	29.00 (28.34)	2.98 (2.96)	
Thiophenol	A	Water/ethanol	92(87)	26.15 (25.87)	2.20 (2.48)	
<i>p</i> -Fluorothiophenol	B	Hexane	81	24.91 (24.51)	1.96 (2.06)	
2-Mercaptonaphthalene	B	Hexane	93	35.41 (35.23)	2.58 (2.69)	
<i>p</i> -Chlorothiophenol	B	Hexane	63	23.66 (23.42)	1.74 (1.96)	
<i>p</i> -Bromothiophenol	A	Hexane/methylene chloride	71	21.10 (20.81)	1.54 (1.74)	
1-Mercaptonaphthalene	B	Hexane	97	35.51 (35.23)	2.70 (2.69)	
<i>o</i> -Mercaptobenzoic acid	A	Hexane/methylene chloride	168(171)	26.08 (26.04)	1.88 (2.18)	

(Continued)

TABLE 1 (contd.)

Parent Acid	Method of preparation ^a	Recryst. solvent	Melting point (°C) ^c	Analysis found (calcd.) (%)		
				C	H	N
2-Mercaptopyridine	A	Water/ethanol	53	22.38 (22.10)	1.90 (2.17)	4.27 (4.30)
2-Mercaptoquinoline	B	Hexane	132	31.54 (31.94)	2.25 (2.42)	3.90 (3.73)
8-Mercaptoquinoline	B	Water/acetone	163	32.18 (31.94)	2.51 (2.42)	3.93 (3.73)
Thiobenzoic acid	B	Water/acetone	61	26.98 (27.22)	2.42 (2.28)	
Pentafluorothiophenol	B	Water/acetone	102	19.77 (20.26)	0.74 (0.73)	
Dithizone (diphenylthiocarbazone)	B	Methanol	144(dec.) (146)	35.06 (35.70)	2.95 (3.00)	11.11 (11.90)
2-Mercaptopyridine- <i>N</i> -oxide	B	Water/ethanol	117	21.14 (21.07)	1.96 (2.07)	4.26 (4.10)
<i>C. X = CO₂</i>						
Myristic acid	B	Methanol	82	40.69 (40.67)	6.88 (6.77)	
<i>p</i> -Hydroxybenzoic acid	B	Hexane/methylene chloride	205(dec.)	27.61 (27.22)	2.24 (2.28)	
<i>trans</i> -Cinnamic acid	B	Water/ethanol	157	33.46 (33.09)	2.56 (2.77)	
Benzoic acid	B	Hexane/methylene chloride	113(110)	28.59 (28.51)	2.33 (2.39)	
Salicylic acid	A	Methanol	118(114)	27.21 (27.22)	1.91 (2.28)	

^a Refer to experimental section for details of the preparations. ^b Sample washed with water, methanol, and ether.

^c Literature values in parentheses.

A, B, or C in Table 1. The crude products were purified by the methods indicated in the table.

Method A involved the use of an aqueous solution of methylmercury hydroxide prepared from methylmercury iodide and an excess amount of freshly precipitated silver oxide. The methylmercury hydroxide solution, from which silver iodide and excess silver oxide had been removed by filtration, was added to a methanolic solution of the organic acid. Equimolar amounts of methylmercury iodide and the acid were taken.

In method B, commercial methylmercury acetate (found to have the correct C and H analyses) was dissolved in water and added to the acid dissolved in methanol or methanolic KOH solution.

A third method of preparation, C, was used to obtain one compound and for repeat preparations of some others. Methylmercury hexacyanocobaltate(III), prepared from methylmercury hydroxide and hexacyanocobaltic acid, was used as the source of methylmercury cations. The organic acid, dissolved in methanol was stirred with the suspended cyanocobaltate at reflux for ca. 48 h after which time a little ether was added and the solids (the etherate of hexacyanocobaltic acid and methylmercury hexacyanocobaltate) were removed. Evaporation of the solvent

TABLE 2

 ^{199}Hg - ^1H COUPLING CONSTANTS FOR CH_3HgXR AND pK VALUES FOR THE ACIDS RXH

No.	Parent acid RXH	pK of RXH		J(¹⁹⁹ Hg- ¹ H)(Hz) ^f in pyridine
		(Calcd.) ^a	(Lit.)	
A. X=O				
1	Phenol	9.92	9.92 ^b	207(206)
2	p-Chlorophenol	9.41	9.38 ^b	210
3	1-Naphthol	9.39	9.39 ^b	210(204)
4	p-Bromophenol	9.32	9.34 ^b	207
5	m-Bromophenol	9.05	9.03 ^d	212
6	o-Bromophenol	8.36	8.42 ^b	217(215)
7	2,4-Dichlorophenol	7.89	7.85 ^a	220
8	8-Hydroxyquinoline	7.7	9.89 ^e	222(221)
9	p-Formylphenol	7.62	7.66 ^b	219
10	p-Nitrophenol	7.16	7.14 ^b	223
11	5-Acetyl-8-hydroxyquinoline	5.89		234(228)
12	Pentafluorophenol	5.86	5.33 ^b	232(218)
B. X=S				
13	Cyclohexylmercaptan	10.75		157(155)
14	p-t-Butylthiophenol	6.96		168(161)
15	p-Methylthiophenol	6.89		167(162)
16	o-Methylthiophenol	6.81		165(159)
17	Thiophenol	6.52	6.52 ^f	168(160)
18	p-Fluorothiophenol	6.39		170(163)
19	2-Mercaptonaphthalene	6.28		170(164)
20	p-Chlorothiophenol	6.01		171
21	p-Bromothiophenol	5.93		170
22	1-Mercaptonaphthalene	5.90		170(162)
23	o-Mercaptobenzoic acid	5.33		171
24	2-Mercaptopyridine	5.27	9.97 ^g	175(173)
25	2-Mercaptoquinoline	5.03	10.21 ^g	179(176)
26	8-Mercaptoquinoline	4.27	8.29 ^g	176(174)
27	Thiobenzoic acid	3.07	2.61 ^a	182(175)
28	Pentafluorothiophenol	2.52		184(172)
29	Dithizone		4.82 ^h	190
	(diphenylthiocarbazone)			
30	2-Mercaptopyridine-N-oxide			191(190)
C. X=CO ₂				
31	Myristic acid	4.96		224(215)
32	Acetic acid	4.76	4.76 ^b	221
33	p-Hydroxybenzoic acid	4.57	4.48 ^b	225
34	trans-Cinnamic acid		4.43 ^b	225
35	Benzoic acid	4.20	4.20 ^b	226
36	Salicylic acid	2.98	2.97 ^b	232

^a Ref. 6, ^b Ref. 13, ^c Values in parentheses measured in chloroform, ^d Ref. 14, ^e Ref. 15, ^f Ref. 16, ^g Ref. 17, ^h Ref. 18.

afforded crystals of the crude salts. This method is useful for the preparation of very soluble methylmercury salts. Also, the methylmercury hexacyanocobaltate provides a fairly safe source of methylmercury cations.

Proton magnetic resonance data were obtained on a Varian Associates Model

A-60 spectrometer using pyridine and, when possible, chloroform as solvents. Although the chemical shifts for the methyl group protons were somewhat dependent on concentration, (giving values that ranged from τ 8.9–9.3), the J values were virtually invariant with changing concentration. The estimated accuracy of the J values is ± 1 Hz.

RESULTS AND DISCUSSION

In Table 2 are listed the coupling constants for the methylmercury salts along with the pK 's of the corresponding acids. The calculated pK values were obtained by the method of Barlin and Perrin⁶. These are seen to compare well with the experimental values where known. For the thiophenols, it was necessary to use the calculated values because there are few experimental pK data available for these acids. The pK values for proton dissociation from each basic site of the dibasic acids were needed. These were also calculated by Barlin and Perrin's method.

The data of Table 2 are presented graphically in Fig. 1, which is a plot of pK vs. the coupling constant, J . Three sets of points, one for each kind of basic site, are obtained. Each set of points follows the straight-line relationship of Evans, Ridout and Wharf¹. Least squares empirical relationships have been derived from the data (omitting spurious points, Nos. 8, 24, 25, 26, 29) which are given in the caption of the figure. The standard deviations S_J , are given in parentheses. For acids of the same pK , the coupling constants decrease in the order: phenolates > carboxylates > thiophenolates. For example, reading from the curves at pK 5 gives $J(\text{CH}_3\text{HgOR})$, 239; $J(\text{CH}_3\text{HgOOCR})$, 222; $J(\text{CH}_3\text{HgSR})$, 175 Hz. This is the order of increasing polarizability of the basic site and increasing covalent character of the Hg-X bond.

In Fig. 2 is shown a plot of J values for CH_3HgOR derivatives vs. J values for the corresponding CH_3HgSR derivatives. Points fit the straight line if each pair of compounds may be represented as containing Hg-S and Hg-O bonds in the thio and oxo analogues, respectively. A least squares equation and the standard deviation, S_J , were obtained omitting point 23,36. These are given in the caption of the figure.

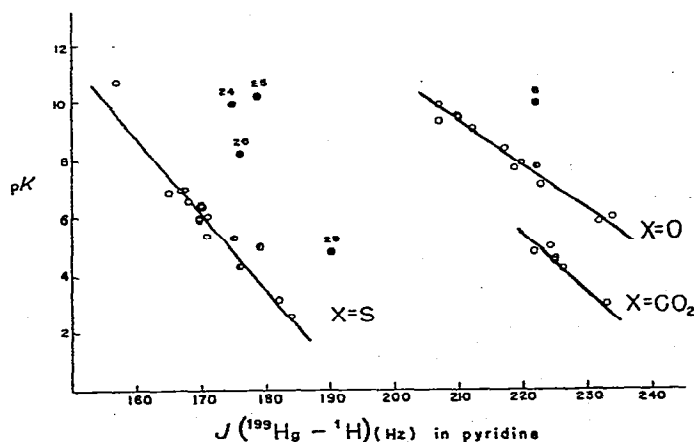


Fig. 1. A plot of $J(^{199}\text{Hg}-^1\text{H})$ for CH_3HgXR against the pK of the parent acid RXH . For CH_3HgOR : $J(^{199}\text{Hg}-^1\text{H}) = 272.8 - 6.76 pK$. ($S_J = 1.4$). For CH_3HgOOCR : $J(^{199}\text{Hg}-^1\text{H}) = 250.2 - 5.72 pK$. ($S_J = 1.5$). For CH_3HgSR : $J(^{199}\text{Hg}-^1\text{H}) = 193.9 - 3.81 pK$. ($S_J = 1.9$).

The graph includes the pair 8-hydroxyquinoline and 8-mercaptoquinoline in which, therefore, the CH_3HgX ($\text{X}=\text{S}$ or O) groups appear to be located at the 8-position in both compounds. That is to say, the mercury atom is not bonded to the quinoline nitrogen atom in either compound.

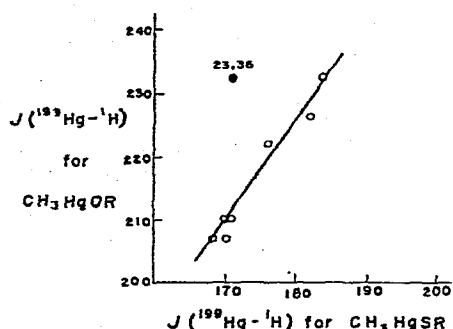


Fig. 2. A plot of $J(^{199}\text{Hg}-^1\text{H})$ for CH_3HgOR against $J(^{199}\text{Hg}-^1\text{H})$ for CH_3HgSR . $J(\text{CH}_3\text{HgOR})=1.57 J(\text{CH}_3\text{HgSR})-57.9$. $J(\text{CH}_3\text{HgSR})=0.636 J(\text{CH}_3\text{HgOR})+36.8$ ($S_f=1.15$).

The point for 8-hydroxyquinoline in Fig. 1 (No. 8) does not fit the line for $\text{X}=\text{O}$. Since it has been suggested by Fig. 2 that the methylmercury salt is most probably a phenolate, the pK value of Fig. 1 must be too high for the curve. That is, the acid appears to be somewhat more stabilized than the methylmercury salt. We attribute this to hydrogen bonding effects in the acid which are not matched by similar interactions in the methylmercury salt. The calculated value of pK , which does not include the effects of hydrogen bonding, gives the point indicated by the half-circle in Fig. 1, $\text{X}=\text{O}$, which fits the line quite well.

The point in Fig. 2 for the derivatives of $o\text{-HOOC}_6\text{H}_4\text{XH}$ (23,36) does not fall on the line suggesting a difference in the structures of the two methylmercury salts. For the methylmercury derivative of salicylic acid, ($\text{X}=\text{O}$), the point of attachment of the methylmercury group appears to be the carboxyl site as is shown by the fact that for $J=232$ Hz, $\text{pK}=2.98$ fits the line for carboxylate derivatives in Fig. 1. However, for the derivative of o -mercaptobenzoic acid, a mercury-sulfur bond is indicated by the low value of J (171 Hz). Thus the bonding preference of methylmercury for sulfur over the carboxylate group in o -mercaptobenzoic acid is revealed by the coupling constants. This is expected behavior.

The mercapto N -heterocyclic compounds listed in Table 3 form methylmercury salts whose J - pK values (Nos. 24, 25 and 26) do not fit the line for $\text{X}=\text{S}$ in Fig. 1. Because the J values are in the expected range for Hg-S bonding, it is believed that the experimental pK 's are too high for the curve. In Table 3 are given the ratios of tautomeric forms for these acids showing that N-H bonding is preferred in the protonated forms. Hence, the experimental pK 's represent proton affinities for the N -atom, not the sulfur sites. If one plots instead the pK values calculated for proton loss from the sulfur sites the points shown as half-circles in Fig. 1 are obtained. These do fit the line. We conclude, therefore, that the proton occupies the nitrogen atom sites (as shown in Table 3) but that the mercury atom is attached to sulfur in the methylmercury derivatives. A study of the UV spectra of phenylmercury derivatives of similar mercapto N -heterocyclic compounds has revealed the same bonding preferences^{7,8}.

TABLE 3

APPROXIMATE RATIOS OF MOLECULES HAVING A HYDROGEN ATOM ON NITROGEN TO THOSE HAVING HYDROGEN ON SULFUR IN SOME MERCAPTO N-HETEROCYCLIC ACIDS

Compound	Ratio of tautomers ^a	
2-Mercaptopyridine	N-H/S-H	49000
2-Mercaptoquinoline	N-H/S-H	140000
8-Mercaptoquinoline	N-H/S-H	27

^a Ref. 9.

The question of chelation to the mercury in some of these compounds is disregarded for the following reasons. The potential chelating thiophenols (Nos. 23, 24, 25 and 26 in Table 2) give J values that are typical of non-chelated (monodentate) thiophenols. An increase in the coordination number of mercury to three or four by chelation and the concomitant decrease in the percent s -character in the hybrid bonds between mercury and the methyl group should lead to a noticeable decrease in J^{11} . This is not observed. Also, the residual Lewis acidity of methylmercury in linearly hybridized covalent compounds has been found to be quite small; the methylmercury cation is considered to have a coordination number of one¹².

It has been shown that a J - pK relationship can be extended to dibasic acid salts if the proper choice of bonding sites is made. Conversely, differences in the structures of protonated and mono-methylmercury salts are revealed by the lack of adherence to the J - pK equation developed for monobasic derivatives where both the proton and methylmercury ions necessarily are attached to the same basic site.

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