A Study of *trans* Influence in Methylmercury(II) Compounds by Means of Vibrational Analysis

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Force constants K(Hg–C) were evaluated for a series of methylmercury compounds: CH_3HgX (X=CH_3, F, Cl, Br, I, CN, SCN, $As(CH_3)_3$, SCH_3, $SHgCH_3$, and $S(HgCH_3)_2$). It was found that K(Hg–C) increases in the following order of X: $S(HgCH_3)_2(1.86) < I(2.27) < SCH_3(2.33) = CH_3(2.330) < As(CH_3)_3(2.37) \leq Br(2.37_7) \leq SHgCH_3(2.38) \leq Cl(2.38_2) < SCN(2.39) < F(2.55) < CN(2.61$ md/Å). This order coincides, except for the cases of CN and $As(CH_3)_3$, with the order of increase in the first ionization potential of X for X=I, SCH_3, CH_3, Br, Cl, and F. Since this effect of X upon K(Hg–C) is regarded as a vibrational *trans* influence, this order was compared with that of the coupling constants in NMR, $J(^{199}Hg\text{-}^{13}C)$ and $J(^{199}Hg\text{-}^{1}H)$, and with the order of the bond-dissociation energy of CH_3HgX into $\cdot CH_3$ and $\cdot HgX$.

A number of organomercuric compounds with the general formula of R–Hg–X have been reported, where R represents an alkyl or aryl group, and X, an inorganic or organic ligand. It is well known that the Hg–C bonding in those compounds is stable and essentially covalent in nature, but it is considerably affected by the ligand, X. Since the C–Hg–X bonding is linear, this effect may be regarded as the "*trans* influence" of the X upon the C–Hg bond. This has been investigated extensively by various methods. For instance, Hatton *et al.*[1] studied the variation in $^{199}Hg\text{-}^{1}H$ geminal coupling constants by varying the ligand, X. Henneike[2] calculated the $^{199}Hg\text{-}^{13}C$ and $^{199}Hg\text{-}^{1}H$ coupling constants by the extended Hückel MO method. Charnley and Skinner[3] evaluated the Hg–C bond-dissociation energies from thermodynamic measurements in the gas phase. The frequencies of the Hg–C stretching vibration and even some force constants, K(Hg–C), have been reported.[4–19] These values, however, have rather limited significance for the discussion of the *trans* influence of methylmercury compounds because, as is well known, the vibrational frequency is not proportional to the force constant, and the available data on force constants, K(Hg–C), were not calculated by the same principle, *e.g.*, using the same valence field and the same assumption of dynamic units in a molecule. Therefore, in the present study, force constants K(Hg–C) were evaluated for a series of methylmercury compounds (CH_3HgX (X=CH_3, F, Cl, Br, I, CN, SCN, $As(CH_3)_3$, SCH_3, $SHgCH_3$, and $S(HgCH_3)_2$) in order to elucidate the *trans* influence of the X upon the Hg–C bond. The numerical data

TABLE 1. BOND LENGTHS(Å) AND BOND ANGLES[a] USED FOR THE CALCULATIONS

$(CH_3)_2Hg$	r(Hg-C)=2.094[22,b]	
CH_3HgF	r(Hg-C)=2.06[23,c]	r(Hg-F)=1.93[d]
CH_3HgCl	r(Hg-C)=2.061[24,b]	r(Hg-Cl)=2.282[24,b]
CH_3HgBr	r(Hg-C)=2.074[24,b]	r(Hg-Br)=2.406[24,b]
CH_3HgI	r(Hg-C)=2.087[25,b]	r(Hg-I)=2.528[25,b]
CH_3HgCN	r(Hg-C)=2.082[26,e,f]	r(Hg-CN)=2.051[26,e,f]
	r(C-N)=1.141[26,e,f]	θ(Hg-C-N)=180[26,e,f]
CH_3HgSCN	r(Hg-C)=2.06[23]	r(Hg-S)=2.50[27]
	r(S-C)=1.58[16]	r(C-N)=1.21[16]
	θ(Hg-S-C)=120[16]	θ(S-C-N)=180[16]
$CH_3HgAs(CH_3)_3^+$	r(Hg-C)=2.06[23]	r(Hg-As)=2.11[g]
	r(As-C)=1.948[29,e,h]	θ(Hg-As-C)=112.8[29,e,h]
CH_3HgSCH_3	r(Hg-C)=2.094[22,b]	r(Hg-S)=2.36[30,e]
	r(S-C)=1.70[30,e]	θ(Hg-S-C)=111[30,e]
$(CH_3Hg)_2S$	r(Hg-C)=2.094[22,b]	r(Hg-S)=2.47[31,i]
	θ(Hg-S-Hg)=105[31,i]	
$(CH_3Hg)_3S^+$	r(Hg-C)=2.09[22,b]	r(Hg-S)=2.47[31,i]
	θ(Hg-S-Hg)=117, 111, and 105[j]	

a) All the θ(C–Hg–X) that are 180° are omitted in this table. b) By microwave. c) Estimated from the tendency for r(Hg–C) to decrease with X=I, Br, and Cl. d) Calculated by r(Hg–X)$-r_c$(X)$+r_c$(F), where X=Cl, Br, and I, and where r_c denotes Pauling's covalent radius. e) By X-ray diffraction. f) By neutron diffraction. g) The r(Hg–As) was calculated by r_c(As)$+r_i(Hg^{2+})-0.18$, assuming that the ionic radius (1.10 Å)[28] of Hg^{2+} in HgX_4^{2-} may be transferred to CH_3HgX molecules and that r_c(As)$+r_i(Hg^{2+})$ may be corrected by -0.18 Å, which is the difference between the observed $r(Pt^{2+}-As)$[29] and the sum of r_c(As)$+r_c(Pt^{2+})$, where r_i denotes the ionic radius. h) Transferred from $Pt_2Cl_4[As(CH_3)_3]_2$, and θ(Hg–As–C) is the mean value of the three angles. i) Calculated based on measurements of the dipole moments of $(CH_3Hg)_2S$, $(C_2H_5Hg)_2S$, and $CH_3HgSHgC_2H_5$. j) The vibrational analyses were carried out for the various assumed θ(Hg–S–Hg)'s under the C_{3v} symmetry.

Table 2. The observed and calculated frequencies (cm^{-1}) of CH_3HgX

Assignments	Obsd (refs)	Calcd	Assignments	Obsd (refs)	Calcd
CH_3HgCH_3			E δ(C-Hg-As)	101 (17)	100.9
asym ν(Hg-C)	550 (4, 5)	550.0	CH_3HgSCN		
sym ν(Hg-C)	515 (4, 5)	515.0	ν(C-N)	2138 (15, 16)	2138.0
δ(C-Hg-C)	156 (4, 5)	156.0	ν(S-C)	792 (15, 16)	792.0
CH_3HgF			ν(Hg-C)	540 (15, 16)	540.0
ν(Hg-C)	561 (6)	561.0	δ(S-C-N)	*ca.* 480 (15, 16)	475.8
ν(Hg-F)	482 (6)	482.0	ν(Hg-S)	283 (15, 16)	283.0
δ(C-Hg-F)	170 (6)	170.0	δ(C-Hg-S)	150[a]	151.6
CH_3HgCl			CH_3HgSCH_3		
ν(Hg-C)	539 (7, 8, 9)	539.0	A′ ν(S-C)	698 (18, 19)	698.0
ν(Hg-Cl)	304 (7, 8, 9)	304.0	A′ ν(Hg-C)	533 (18, 19)	533.0
δ(C-Hg-Cl)	112 (7, 8, 9)	112.0	A′ ν(Hg-S)	329 (18, 19)	329.0
CH_3HgBr			A′ δ(Hg-S-C)	192 (18, 19)	192.0
ν(Hg-C)	538 (7, 8, 10, 11)	538.0	A′/A″ δ(C-Hg-S)	133 (18, 19)	126.0 (A″)
ν(Hg-Br)	202 (7, 8, 10, 11)	202.0			113.1 (A′)
δ(C-Hg-Br)	100 (7, 8, 10, 11)	100.0	$(CH_3Hg)_2S$		
CH_3HgI			B_2 ν(Hg-C)	530	528.0
ν(Hg-C)	526 (7, 8, 11—13)	526.0	A_1 ν(Hg-C)	525	527.0
ν(Hg-I)	173 (7, 8, 11—13)	173.0	B_2 ν(Hg-S)	344	344.0
δ(C-Hg-I)	97 (7, 8, 11—13)	97.0	A_1 ν(Hg-S)	300	300.0
CH_3HgCN			A_1/B_2 δ(C-Hg-S)	137	134.0 (B_2)
ν(C-N)	2180 (14)	2180.0			131.3 (A_1)
ν(Hg-CH_3)	565 (14)	565.0	A_1 δ(Hg-S-Hg)	80	77.0
ν(Hg-CN)	386 (14)	386.0	$(CH_3Hg)_3S^+$ ($\theta=105°$)		
δ(Hg-C-N)	306 (14)	303.1	E′ ν(Hg-C)	534	534.6
δ(C-Hg-CN)	75 (14)	73.3	A_1 ν(Hg-C)	529	529.4
$CH_3HgAs(CH_3)_3^+$			E′ ν(Hg-S)	329	327.4
E ν(As-C)	632 (17)	632.0	A_1 ν(Hg-S)	258	257.5
A_1 ν(As-C)	598 (17)	598.0	A_1/E' δ(C-Hg-S)	127	131.1 (E′)
A_1 ν(Hg-C)	537 (17)	537.0			130.1 (A_1)
A_1 ν(Hg-As)	253 (17)	253.0	A_1/E' δ(Hg-S-Hg)	86	126.5 (E′)
E δ(C-As-C)	219 (17)	219.0			73.7 (A_1)
A_1 δ(C-As-C)	167 (17)	167.0			

a) Assumed from the δ(C-Hg-S) values of the CH_3HgSCH_3, $(CH_3Hg)_2S$, and $(CH_3Hg)_3S^+$.

Table 3. Force constants (md/Å) of CH_3HgX

MeHgMe	K(Hg-C) 2.330		H(C-Hg-C) 0.0928	E(C···C) 0.010			
MeHgF	K(Hg-C) 2.55	K(Hg-F) 2.43	H(C-Hg-F) 0.123				
MeHgCl	K(Hg-C) 2.38_2	K(Hg-Cl) 1.67	H(C-Hg-Cl) 0.063				
MeHgBr	K(Hg-C) 2.37_7	K(Hg-Br) 1.41	H(C-Hg-Br) 0.056				
MeHgI	K(Hg-C) 2.27	K(Hg-I) 1.41	H(C-Hg-I) 0.053				
MeHgCN	K(Hg-C) 2.61	K(Hg-CN) 2.13	H(C-Hg-CN) 0.033	K(C-N) 17.47	H(Hg-C-N) 0.105		
$MeHgAsMe_3^+$	K(Hg-C) 2.37	K(Hg-As) 1.53	H(C-Hg-As) 0.084	K(As-C) 2.75	H(C-As-C) 0.140	F(Hg···C) 0.098	F(C···C) 0.034
MeHgSCN	K(Hg-C) 2.39	K(Hg-S) 1.50	H(C-Hg-S) 0.11	K(C-N) 15.38	K(S-C) 5.87	H(S-C-N) 0.29	
MeHgSMe	K(Hg-C) 2.33	K(Hg-S) 1.52	H(C-Hg-S) 0.078		K(S-C) 2.90	H(Hg-S-C) 0.183	
$(MeHg)_2S$	K(Hg-C) 2.38	K(Hg-S) 1.46	H(C-Hg-S) 0.118	H(Hg-S-Hg) 0.15	F(Hg···Hg) 0.0		
$(MeHg)_3S^+$ ($\theta=105°$)	K(Hg-C) 1.86	K(Hg-S) 0.79	H(C-Hg-S) 0.06	H(Hg-S-Hg) 0.06	F(Hg···Hg) 0.30	F(C···S) 0.48	

TABLE 4. THE K(Hg-C), ν(Hg-C), IONIZATION POTENTIALS (IP), COUPLING CONSTANTS ($J(^{199}Hg-^{1}H)$), AND BOND-DISSOCIATION ENERGIES (D) OF CH_3HgX COMPLEXES

X	K(Hg-C) md/Å	ν(Hg-C) cm^{-1}	IP[32] eV	$J(^{199}Hg-^{1}H)$[1] Hz	D[3,a] kcal/mol
F	2.55	561	17.42	—	—
CN	2.61	565	14.1	176	—
SCN	2.39	540	—	208	—
Cl	2.38_2	539	13.01	215.8	63.8±2.9
Br	2.37_7	538	11.84	212	61.3±2.8
$S(HgCH_3)_2$	1.86	538 529	—	—	—
I	2.27	526	10.45	200	58.5±3.1
$SHgCH_3$	2.38	530 525	—	156.6	—
CH_3	2.330	550 515	9.95	100.6	51.5±2
SCH_3	2.33	533	9.84[b]	—	—
$As(CH_3)_3$	2·37	537	8.3	180	—

a) $CH_3HgX \rightarrow \cdot CH_3 + \cdot HgX$ in the gas phase at 20 °C. b) Transferred from the IP of CH_3SH.

on the IR and Raman spectra used for the calculations were taken from the literature[4-19] except for $X=SCH_3$, $SHgCH_3$ and $S(HgCH_3)_2$, the data of which are obtained in this work. Some features of these IR and Raman spectra reduced from the assignments are described.

Experimental

The numerical data of the IR and Raman spectra used for the present calculations were taken from the literature[4-19] except for the following three samples, which were prepared according to the literature[20,21] and well confirmed by measurements of the mp and by elemental analysis of mercury:

CH_3HgSCH_3: mp 25 °C (lit,[20] 25 °C).

$(CH_3Hg)_2S$: mp 145 °C (lit,[20] 145 °C). Found: Hg, 85.6%. Calcd: Hg, 86.6%.

$(CH_3Hg)_3SClO_4$: mp 144 °C (lit,[21] 143 °C). Found: Hg, 77.63%. Calcd: Hg, 77.31%.

The infrared spectra of CH_3HgSCH_3, $(CH_3Hg)_2S$ and $(CH_3Hg)_3SClO_4$ were recorded with KBr disks from 300 to 4000 cm^{-1} and with Nujol mulls on polyethylene sheet from 30 to 600 cm^{-1} at 23 °C. The infrared spectra of $(CH_3Hg)_2S$ and $(CH_3Hg)_3SClO_4$ were recorded from 200 to 600 cm^{-1} with polyethylene matrices at 77 K. The instruments used were a JASCO-403G grating IR spectrometer and a HITACHI FIS-3 grating far-IR spectrometer. The Raman spectra of $(CH_3Hg)_3SClO_4$ were recorded in the powder state and in a saturated aqueous solution (about 15 wt%) with a JEOL JRS-O2AS and a JRS-S1 Raman spectrometer equipped with an Ar^+-ion laser as a source.

Calculations

The vibrational analysis was carried out using the Urey-Bradley field. The methyl group was treated as a dynamic unit. The bond lengths and bond angles used for the calculations are listed in Table 1 along with the references.

Results and Discussion

The IR and Raman spectra of CH_3HgSCH_3 have previously been reported.[18,19] The IR spectrum of $(CH_3Hg)_2S$ has been reported only in the NaCl region,[20] and so the IR spectrum in a region lower than 650 cm^{-1} was measured in this study. Its Raman spectrum could not be recorded, because $(CH_3Hg)_2S$ decomposed into HgS within one minute after exposure to the Ar^+-ion laser beam. The spectra and their assignments will be reported in a separate paper. Here the description will be limited to some tendencies reduced from the assignments of the bands for CH_3HgSCH_3, $(CH_3Hg)_2S$, and $(CH_3Hg)_3SClO_4$: a) the asymmetric deformation, the symmetric deformation, and the rocking vibrations of the methyl group appear at 1404, 1177, and 768 cm^{-1} respectively, when the methyl group is attached to the mercury atom, and at 1431, 1310—1284, and 955 cm^{-1} when it is attached to the sulfur atom; b) the Hg–C stretching vibration of CH_3–Hg is found at 515—565 cm^{-1}; c) the Hg–S stretching bands of $(CH_3Hg)_2S$ split into four under the influence of the lattice field, though there should be two; therefore the values of (354+334)/2 and (310+291)/2 cm^{-1} are used for the calculations as the antisymmetric and symmetric Hg–S stretching frequencies respectively.

As may be seen in Table 2, a satisfactory agreement between the calculated and experimentally observed frequencies is obtained. The force constants are summarized in Table 3. Arranging the X of CH_3HgX in an increasing order of K(Hg–C), a vibrational *trans* influence series is obtained, where the numerical values of K(Hg–C) are written in parentheses in md/Å units: $S(HgCH_3)_2(1.86) < I(2.27) < SCH_3(2.33) = CH_3(2.330) < As(CH_3)_3(2.37) < Br(2.37_7) \leq SHgCH_3(2.38) \leq Cl(2.38_2) < SCN(2.39) < F(2.55) < CN(2.61)$.

On the other hand, the K(Hg–C) of CH_3HgX in the generalized valence field increase in the following order of X: I(2.290 md/Å)[12] < Cl(2.42)[9] < Br(2.48)[10] according to Meić[9,10,12] and Randić,[9,10] or I(2.50 md/Å) < Br(2.60) < CN(2.78) according to Goggin and Woodward.[13] Since not only the values of K(Hg–C) but also the order of X thus depend upon the types of the potential function, the recalculation in this work is regarded as significant for the investigation of

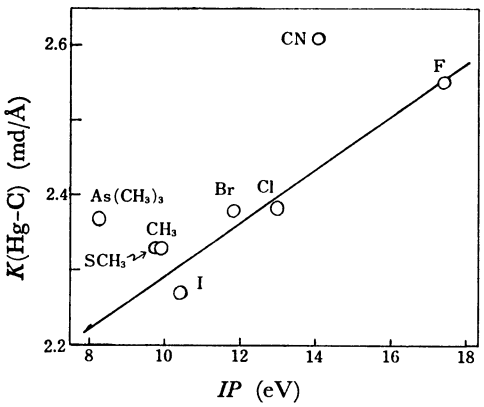

Fig. 1. Relation between K(Hg–C) and the ionization potentials of X.

the *trans* influence.

Let us now discuss the factor which will determine the K(Hg–C). As may be seen in Fig. 1, a linear relationship is found between K(Hg–C) and the first ionization potential, *IP*, of X for this series, except in the cases of X=CN and $As(CH_3)_3$, whose K(Hg–C) values are considerably larger than those to be expected from the linearity. The increase in K(Hg–C) with the increase in the first ionization potential of X can be explained in terms of the inductive effect of X through the σ path. On the other hand, the deviation in the linearity may be ascribed to the π-back donation from the mercury to the arsine group.

Some previously reported data may be referred to in order compare them with the presented vibrational *trans*-influence order (Table 4). The order of K(Hg–C) is considerably different from that of $J(^{199}Hg–CH_3)$[1,2]: $CH_3 < SHgCH_3 < CN < As(CH_3)_3 < I < SCN < Br < Cl$. Particularly, cyanide changes its position extremely between K(Hg–C) and $J(^{199}Hg–CH_3)$. The K(Hg–C) increases parallel to the increase in the bond-dissociation energy.[3] It is worthwhile to refer the present results to the well-known *trans*-effect series established in Pt(II) complexes, where CN<I<Br<Cl.[33] Thus, the presently obtained *trans*-influence series for methylmercury compounds is unique in the position of CN.

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