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VIBRATIONAL SPECTRA OF RCH_2HgX- AND $(RCH_2)_2Hg$-TYPE ORGANOMERCURY COMPOUNDS*

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SUMMARY

A study of organomercury compounds is reported. The IR and Raman spectra were measured and frequency assignments are made for 21 compounds. The characteristic frequencies of the $-CH_2HgX$ and the $-CH_2HgCH_2-$ groups were determined and inferences are made on the molecular structure. Normal coordinate analysis was performed for diethylmercury, allylmercury chloride, allylmercury bromide, dibenzylmercury and benzylmercury chloride, bromide and iodide. The force constants in the environment of the Hg atom were refined by the least-squares method. It was found that the force constants of the C–Hg stretching vary in the range from 2.53 to 2.67 mdyn/Å.

INTRODUCTION

The organomercury compounds have become of ever increasing importance in the theoretical studies of organic chemistry. The physico-chemical properties of these compounds have been extensively investigated. On the other hand, the vibrational spectra of this system have scarcely been studied yet.

The investigations reported so far have covered only the infrared and Raman spectra of diethyl mercury[1-4], some low frequency spectra of ethyl- and n-propylmercury bromide[5] and the infrared spectra of allylmercury halides[6].

In this work infrared and Raman spectra of $(C_2H_5)_2Hg$, $CH_2{=}CHCH_2HgX$ ($X{=}Cl$, Br), $C_6H_5CH_2HgX$ ($X{=}Cl$, Br, I), $(C_6H_5CH_2)Hg$ and *o*-$ClC_6H_4CH_2HgCl$ and the infrared spectra of C_2H_5HgBr, n-C_3H_7HgBr, $(CH_2{=}CHCH_2)_2Hg$, *o*-$FC_6H_4CH_2HgX$ ($X{=}Cl$, Br), *o*-CH_3-$C_6H_4CH_2HgCl$, *m*-Y-$C_6H_4CH_2HgCl$ ($Y{=}F$, Cl, Br, CH_3) and *p*-Y-$C_6H_4CH_2HgCl$ ($Y{=}F$, Cl, CH_3) in the range from 200 to 3300 cm^{-1} are discussed. Some of the experimental data have already been published[7-9].

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* Abstracted in part from the Ph.D. dissertation of J. Mink, Moscow State University, 1968. Presented in part at the 1969 Fourth International Conference on Organometallic Chemistry, Bristol, England (Paper B 8).

TABLE 1

GROUP FREQUENCIES OF RCH_2HgX- AND $(RCH_2)_2Hg$-TYPE ORGANOMERCURY COMPOUNDS

Compounds	Phase of measurement[a]	Frequency (cm^{-1})[b]										
		$\delta(CHgX)^c$ $\delta(CHgC)$	$\delta'(CHgX)^c$ $\delta'(CHgC)$	$\delta(CCHg)$	$\nu(HgX)^c$ $\nu_s(CHg)$	$\nu(CHg)^c$ $\nu_{as}(CHg)$	$r(CH_2)$	$t(CH_2)$	$w(CH_2)$	$b(CH_2)$	$\nu_s(CH_2)$	$\nu_{as}(CH_2)$
CH_3CH_2HgBr	s				209	513	690	1186	1237	1410	2850	2975
$(CH_3CH_2)_2Hg$	s, sn, l, g	85	140	212	488	535	634	1179	1232	1424	2846	2953
				259			671	1200				
$CH_3CH_2CH_2HgBr$	s				214	514	688	1178	1280	1430	2845	2960
$CH_2{=}CHCH_2HgCl$	s, sn	(49)	(61)	227	329	504	772	1119	1186	1437	2923	2982
$CH_2{=}CHCH_2HgBr$	s, sn	(36)	(37)	235	206	496	768	1111	1188	1436	2923	2982
$(CH_2{=}CHCH_2)_2Hg$	l			(190)	475	495	718	1075	1191	1424	2907	2960
				(230)			758	1095				
$C_6H_5CH_2HgCl$	s, sn	(38)	(49)	162	326	582	812	1157	1210	1409	2933	2970
$C_6H_5CH_2HgBr$	s, sn, l	(36)	(29)	167	232	580	809	1155	1209	1405	2933	2971
$C_6H_5CH_2HgI$	s, sn	(33)	(23)	162	172	573	809	1156	1209	1408	2932	2972
$(C_6H_5CH_2)_2Hg$	s, sn	(60)	126	126	560	578	811	1154	1208	1410	2911	2945
			172				833					
o-$FC_6H_4CH_2HgCl$	s, sn				335	595	773	1126	1194	1421	2937	2978
o-$FC_6H_4CH_2HgBr$	s				206	596	770	1135	1199	1423		
o-$CH_3C_6H_4CH_2HgCl$	s				306	596	761	1140	1214	1411		
o-$ClC_6H_4CH_2HgCl$	s, sn			172	332	594	784	1140	1211	1411	2921	2956
m-$FC_6H_4CH_2HgCl$	s				296	(?)	825	1152	(?)	1430		
m-$CH_3C_6H_4CH_2HgCl$	s				300	600	830	1165	1215	1420		
m-$ClC_6H_4CH_2HgCl$	s				300	604	820	(?)	1212	1425		
m-$BrC_6H_4CH_2HgCl$	s				349	603			1213	1435		
p-$FC_6H_4CH_3HgCl$	s				298	573	830		1210	1415		
p-$CH_3C_6H_4CH_2HgCl$	s				309	580	828		1210	1420		
p-$ClC_6H_4CH_2HgBr$	s				217	574	837	1135	1215	1411		

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[a] The bands specified in the table were observed in the spectra of gas (g), liquid (l), solution (sn) in CS_2, C_6H_6 or crystalline (s) samples. [b] The symbols ν, δ, r, t, w, b, $_s$, $_{as}$ stand for the stretching, deformation, rocking, twisting, wagging, bending, symmetric and asymmetric vibrations, respectively. The calculated values are in parentheses. [c] The upper symbols refer to the RCH_2HgX- and the lower to the $(RCH_2)_2Hg$-type compounds.

EXPERIMENTAL

The infrared spectra were measured in the range from 200 to 400 cm^{-1} by IKS-21, single beam spectrometer using CsI prism, while in the range from 400 to 3300 cm^{-1} by UR-10 double beam spectrometer with KBr, NaCl and LiF prisms. The Raman spectra were measured by DSF-12 grating spectrograph equipped with photoelectric detector.

The purity of the compounds was checked by C and H analysis and other known physical constants.

RESULTS AND DISCUSSION

Group frequencies

The compounds studied in the present investigation contain either a $-CH_2HgX$, or a $-CH_2HgCH_2-$ group, the vibrations of which could be associated with 11 characteristic frequencies of the observed spectra. The frequencies assigned to the vibrations of these groups are specified in Table 1 and the wavelength intervals in which they were observed are shown in Fig. 1. The CCHg atoms in the RCH_2HgX molecules are assumed to form a planar configuration and the frequencies are analysed relative to this local symmetry. For simplicity, the CCHgCC skeleton is taken to form a single plane in the $(RCH_2)_2Hg$ compounds.

Theoretically, the in-plane or out-of-plane deformation frequencies, $\delta(CHgX)$, of CHgX are expected to appear below 70 cm^{-1}. These low frequencies could not be observed by the present technique, therefore they are omitted. The in-plane and

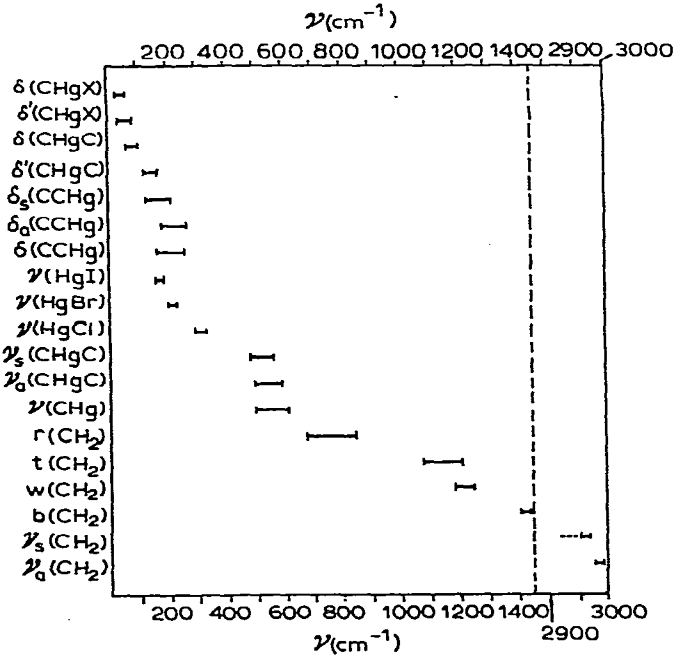

Fig. 1. Group frequencies of RCH_2HgX- and $(RCH_2)_2Hg$-type organomercury compounds.

out-of-plane deformation frequencies of CHgC, δ(CHgC) and δ'(CHgC), are expected to appear below 100 cm^{-1} and at 120–150 cm^{-1}, respectively, being shifted with larger R groups to lower wave numbers.

A similar tendency was observed in the vibrational frequency of the CCHg angular deformation, δ(CCHg). The bands which could be attributed to δ(CCHg) deformation frequencies were observed for $CH_2{=}CHCH_2HgX$ at 230 cm^{-1}, while for $C_6H_5CH_2HgX$ at 170 cm^{-1}. For $(C_2H_5)_2Hg$ the frequencies at 259 and 212 cm^{-1} were assigned to asymmetric and symmetric deformations and they appeared in the spectrum of $(C_6H_5CH_2)Hg$ at 172 and 126 cm^{-1}.

The stretching vibrations, ν(HgCl) and ν(HgBr), could be associated with the frequencies observed at 349–296 cm^{-1} and 232–206 cm^{-1}, respectively. The frequency at 172 cm^{-1} in the spectrum of $C_6H_5CH_2HgI$ was assigned to ν(HgI).

The CHg stretching frequencies, ν(CHg), were found to be typical for each compound, varying within a rather wide interval (from 488 to 604 cm^{-1}).

The rocking, $r(CH_2)$, and twisting, $t(CH_2)$, frequencies of the four deformation vibrations of the methylene groups were observed in wide ranges (634 to 837 cm^{-1} and 1070 to 1200 cm^{-1}, respectively) at considerably varying intensities.

Bands which could be attributed to the wagging, $w(CH_2)$, and bending, $b(CH_2)$, frequencies of the methylene groups appeared in more restricted intervals, 1186–1237 cm^{-1} and 1405–1437 cm^{-1}, respectively, the former being of varying, the latter always of high intensity.

The CH stretching frequencies, ν(CH), of the methylene groups were observed, as expected, in the intervals of 2845–2937 cm^{-1} and 2945–2982 cm^{-1} which could be attributed to symmetric and asymmetric stretching, respectively. It is of interest to note that the CH_2 stretching frequencies of the symmetric $(RCH_2)_2Hg$ organomercury compounds appear always at lower wavelengths than those of the RCH_2HgX type compounds.

Molecular structure

An attempt was made to determine the molecular structure of some of the organomercury compounds from the comparison of the spectra taken at different temperatures with the results of normal coordinate analysis.

(*a*) For the symmetric $(RCH_2)_2Hg$ compounds the calculations confirmed the observation that no coupling exists between most of the vibrations across the Hg atom. Only four of the vibration modes, namely the deformation, δ(CCHg), of the CCHg angle, the stretching, ν(CHg), the rocking, $r(CH_2)$, and the twisting, $t(CH_2)$, vibration of the methylene groups exhibit a splitting due to the interactions across the central Hg atom (see *e.g.* Fig. 2.). The calculations showed that the δ(CCHg) and ν(CHg) vibrations split because of kinematic interactions, while the observed frequencies assigned to the deformation vibrations of the methylene groups could be fitted only by introducing interaction force constants. The values of the force constants were found to be $\pm(0.03 \text{ to } 0.01) \times 10^{-11}$ dyn·cm, which are extremely low. To reduce the difference between the observed and the predicted frequencies assigned to CHg stretching, the force constants of the interactions between the two CHg valence coordinates were taken to be -0.07 and -0.04×10^5 dyn·cm.

The vibrational spectra indicate that in these compounds the linear CHgC skeleton is predominant. It follows that the free rotation is around the CHgC axis,

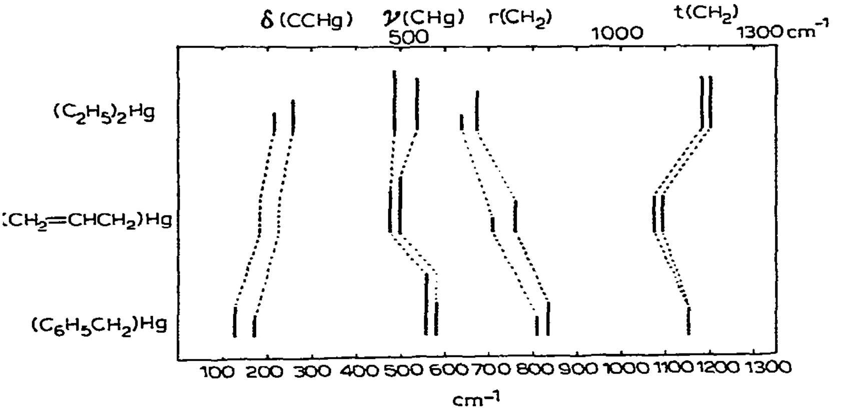

Fig. 2. The splitting modes of $(RCH_2)_2Hg$-type compounds due to the interaction across the central mercury atom.

and the symmetry of the $(RCH_2)_2Hg$ molecule as a whole, can be inferred only from the investigation of the δ(CCHg), ν(CHg), r(CH_2) and t(CH_2) bands.

The selection rules, however, do not enable one to decide unambiguously between the C_2, C_{2v}, C_{2h} or $D_{\infty h}$ symmetries. The spectra can be interpreted in most cases by assuming the simultaneous presence of different configurations. The frequencies were computed assuming C_{2v} or C_{2h} configurations (see Fig. 3.) using in both cases the same force field. The CCHg angular deformation vibration was found to be very sensitive to the change in configuration. This is apparent from the data for diethyl- and dibenzylmercury (Table 2). The change of the CHg stretching frequency practically does not reflect the change in the molecular configuration. The low temperature Raman spectrum of crystalline diethylmercury does not display the band at 259 cm^{-1} which is well observed in the liquid phase, while the rest of the vibrational spectrum seems to be unchanged. This suggests the stabilization of the C_{2h} configuration, though no dominant configuration can be established in the liquid or gas phase. Owing to the apparent decomposition of dibenzylmercury and even more in case of dialkyl mercury compounds during Raman spectroscopy, only a few experimental data can be obtained which do not permit any conclusions to be drawn about the molecular configuration.

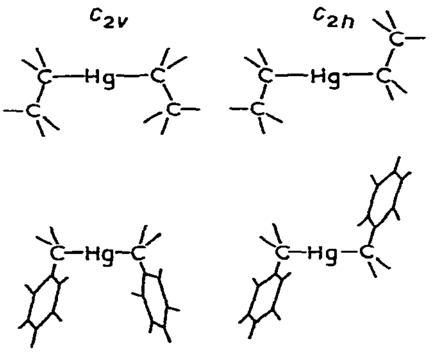

Fig. 3. The chosen configuration of $(C_2H_5)_2Hg$ and $(C_6H_5CH_2)Hg$ for calculation.

TABLE 2

EXPERIMENTAL AND COMPUTED FREQUENCIES FOR DEFORMATION VIBRATIONS OF CCHg VALENCE ANGLES

Compound	Experimental frequencies (cm^{-1})							Computed freqs. (cm^{-1})		Assignment
	Infrared liquid	Raman								
		Liquid					Cryst.	C_{2h}	C_{2v}	
$(CH_3CH_2)_2Hg$	262 s^4	212 m^1	209 m^4	?^{a}	212 m	0.28^a	218 s	222	240	δ_s(CCHg)
	267 s	259 m,s^1	255 s^4	0.4^a	257 s	0.25^a		256	236	δ_{as}(CCHg)
$(C_6H_5CH_2)_2Hg$					123 w^b		126 w	123	156	δ_s(CCHg)
							172 v,w	172	140	δ_{as}(CCHg)

^{a} Polarisation data. ^{b} Solution in dioxane.

(*b*) In organomercuric halogenides (RCH_2HgX) the presence of rotational isomers seems to be probable due to the hindered internal rotation around the C–C bond adjacent to the C–Hg bond. The vibrational spectra of the allylmercury and the benzylmercury halogenides suggest the existence of only one of the configuration both in the crystalline as well as in the dissolved state. To be able to select the most probable configuration, a normal coordinate analysis was performed for CH_2=$CHCH_2HgCl$ with respect to three (*cis*-, intermediate-, *trans*-) and for $C_6H_5CH_2HgCl$ with respect to two (planar-, nonplanar-) configurations (see Fig. 4).

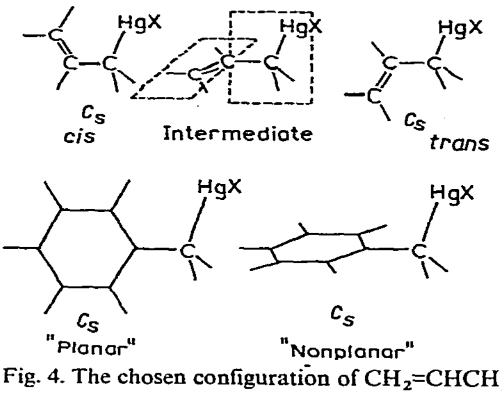

Fig. 4. The chosen configuration of CH_2=$CHCH_2HgCl$ and $C_6H_5CH_2HgCl$ compounds for calculation.

The frequencies which were found to be the most sensitive to changes of configuration are listed in Table 3. The configuration dependence is seen to be very marked in both cases for the ν(CHg) frequencies. The agreement between the observed and predicted frequencies as well as geometric considerations suggest that the allylmercury halogenides have an intermediate, and the benzylmercury halogenides a non-planar configuration.

In the infrared spectrum of crystalline n-C_3H_7HgBr, the appearance of 18 intense bands in the range of 400–1400 cm^{-1}, instead of the expected 12 fundamentals, indicates the possible coexistence of two *gauche*- and *trans*-configurations in the crystalline phase, a phenomenon which is now under more extensive investigation.

TABLE 3

THE MOST SENSITIVE COMPUTED FREQUENCIES FOR SEVERAL CONFIGURATIONS OF $CH_2{=}CHCH_2HgCl$ AND $C_6H_5CH_2HgCl$

Assignment	Exp. freq. ν (cm^{-1})	Computed frequency (cm^{-1})		
		cis	Intermed.	*trans*
$CH_2{=}CHCH_2HgCl$				
δ(CCHg) (angle deform.)	227	138 *A'*	232	193 *A'*
δ(CCC) (angle deform.)	387	406 *A'*	376	314 *A'*
ν(CHg) (CHg stretching)	504	628 *A'*	473	632 *A'*
w(CH) (out-of-plane CH deform.)	683	520 *A''*	640	511 *A''*
$r(=CH_2)$ ($=CH_2$ rocking)	1039	1073 *A'*	1040	1092 *A'*
$w(CH_2)$ (CH_2 wagging)	1186	1237 *A'*	1196	1200 *A'*
		"Planar"	"Nonplanar"	
$C_6H_5CH_2HgCl$				
δ(CCHg) (angle deform.)	162	153 *A'*	162 *A'*	
ν(HgCl) (HgCl stretching)	326	320 *A'*	333 *A'*	
ν(CHg) (CHg stretching)	582	701 *A'*	599 *A'*	
$r(CH_2)$ (CH_2 rocking)	812	864 *A''*	889 *A''*	
$t(CH_2)$ (CH_2 twisting)	1157	1168 *A''*	1154 *A''*	

Force field

The evaluation of the force field in the organomercury compounds has been restricted so far to the methyl derivatives $(CH_3)_2Hg$[10], CH_3HgX (X=Cl, Br, I, CN)[11,12].

The normal coordinate analysis, assuming different configurations, was performed for $(C_2H_5)_2Hg$, CH_2CHCH_2HgX (X=Cl, Br), $C_6H_5CH_2HgX$ (X=Cl, Br, I) and $(C_6H_5CH_2)_2Hg$ using the method developed by Eljashevich, Stepanov[13], Wilson[14] and Mayants[15] with GVFF. The atomic distances and the force constants in zero approximation were taken to be those reported on the corresponding RCH_2X type halogen derivatives (*e.g.* ref. 16). The CHg and HgX bond distances were taken to be equal to the values observed for dimethyl mercury and methyl mercury halogenides[17].

The force constants in the environment of the Hg atom were refined by the least-squares method. Some of the characteristic force constants are listed in Table 4. along with those reported for methyl derivatives[10-12]. The vibrations and force constants of the organic part of the molecules are only slightly affected by the halogen atoms. The force constant of the HgX stretching frequency decreases in the order Cl, Br and I.

The stretching vibration of the C–Hg bond is observed in a wide range of frequencies (488–582 cm^{-1}) while the calculated F(CHg) force constants hardly differ from one another. It would be therefore misleading to take the observed frequency to be a measure of the C–Hg bond strength. The difference in the carbon–mercury frequencies arise from the G-matrix. The calculated values of the eigenvectors show that the CHg stretching vibration leads to considerable angular deformations and that is why the geometry of the environment of Hg atoms is markedly reflected by the calculated values of the CHg frequencies.

TABLE 4

SOME CHARACTERISTIC FORCE CONSTANTS OF ORGANOMERCURY COMPOUNDS

Compound	Force constant (mdyn/Å)		
	F(CHg)	F(HgX)	F(CH)[a]
CH_3HgCl[11]	2.69	2.01	4.96
CH_3HgBr[11]	2.60	1.80	4.93
CH_3HgI[11]	2.50	1.55	4.89
CH_3HgCN[11,12]	2.78	2.16	4.95
$(CH_3)_2Hg$[10]	2.45		4.63
$(C_2H_5)_2Hg$	2.66		5.01
$CH_2{=}CHCH_2HgCl$	2.67	1.93	5.18
$CH_2{=}CHCH_2HgBr$	2.62	1.84	5.18
$C_6H_5CH_2HgCl$	2.63	1.92	5.18
$C_6H_5CH_2HgBr$	2.62	1.83	5.18
$C_6H_5CH_2HgI$	2.60	1.48	5.18
$(C_6H_5CH_2)_2Hg$	2.53		5.18

[a] CH stretching force constants of CH_2 (or CH_3) group next to the mercury atom.

In the ethyl, benzyl and allyl derivatives the force constants of the carbon–hydrogen stretching frequency in the methylene group next to the mercury atom varied in a narrow interval around 5.13±0.05 mdyn/Å.

The values of the most characteristic force constants varied in the intervals given in Table 5. Here the data reported for the methyl derivatives were also used.

TABLE 5

MOST CHARACTERISTIC FORCE CONSTANTS OF RCH_2HgX- AND $(RCH_2)_2Hg$-TYPE ORGANOMERCURY COMPOUNDS

Type of compound	Force constants (mdyn/Å)		Type of R
	F(CHg)	F(HgX)	
RCH_2HgCl	2.66±0.03	1.96±0.04	H[11,12], $CH_2{=}CH$, C_6H_5
RCH_2HgBr	2.62±0.01	1.83±0.02	
RCH_2HgI	2.55±0.05	1.52±0.03	
$(RCH_2)_2Hg$	2.54±0.11		H[10], CH_3, C_6H_5

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