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Solvent Effect on the Raman Spectra of Mercury(II) Halides

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Synopsis. Raman spectra show that the Hg-X bond strengths in mercury (II) halides are remarkably weakened by the interaction with certain solvents. Relations between the degree of this weakening and (a) the Lewis basicity (Gutmann's donor number) of the solvent and (b) the ionic character of the Hg–X bond are pointed out, together with a simple explanation.

The Raman spectra of $HgCl_2$ in a number of organic solvents have been studied by Allen and Warhurst[1] and it was found that the frequency of the Cl–Hg–Cl stretching vibration is remarkably influenced by the nature of the solvent. They discussed their results chiefly on the basis of the dielectric constants of the solvents.

We have tried to study this kind of solvent effect further, using a larger variety of solvents, and comparing the obtained results with those of other halides, cyanide and methyl halides of mercury(II).

Experimental

Use was made of a JEOL-S1 Raman Spectrophotometer and an Argon laser (5145 Å). All the reagents (including solvents) used were Extra Pure or Spectro grade chemicals. Since the solubilities of the mercury(II) compounds in many of the solvents are low, the concentrations in many cases were much below 0.1 M.

Results and Discussion

The observed frequencies (ν) of the X–Hg–X symmetrical stretching vibration for the HgX_2 molecules are shown in Table 1,* and those of the Hg–X and Hg–CH_3 stretching frequencies for the CH_3HgX molecules in Table 2. The values of the apparent force constants(k) of the bonds, calculated by means of simple valence force models,[2] are also given. The ν values of $HgCl_2$ reported by Allen and Warhurst[1] were in general confirmed, except that in dioxane for which they reported 302 cm^{-1}.

The data in Table 1 clearly show that the ν and k values of a halide, *i.e.* the strength of the Hg–X bond in it, decrease in the order gas>benzene>acetone>water>methanol>dimethylformamide (DMF)>pyridine or, roughly speaking, with the increase of the coordination ability (Lewis basicity) of the solvent. It is also clear that the rates of this decrease are in the order $HgCl_2 > HgBr_2 > HgI_2$. This is the same as the order of the decrease of the ionic characters of Hg–X bonds which are estimated (from the classical electronegativity scale of Pauling) to be: Hg–Cl 26%, Hg–Br 19%, Hg–I 9%.

If we plot the values of k of the halides against the donor number (DN) of Gutmann,[3] which serves as a simple measure of the Lewis basicity of a solvent, these relations can be very clearly recognized. The results are shown in Fig. 1.

In the case of the methyl halides in Table 2,** there are also similar decreases of ν and k from methanol to pyridine, and the rates of this decrease are again in the order of chloride>bromide>iodide. However, it can

Table 1. Raman frequencies of HgX_2 (cm^{-1}) and apparent force constants of Hg–X bonds ($\times 10^5$ dyn cm^{-1})

	Gas[a]	Benzene	Nitromethane	Nitrobenzene	Benzonitrile	Acetonitrile
$HgCl_2$	335—360	340 (2.42)	335 (2.35)	335 (2.35)	330 (2.28)	330 (2.28)
$HgBr_2$	220—225	—	208 (2.05)	—	—	206 (2.01)
HgI_2	156	—	—	—	—	148 (1.64)
	Methyl Acetate	Acetone	Ethyl Acetate	Water	Methanol	Ethanol
$HgCl_2$	329 (2.27)	330 (2.28)	333 (2.33)	322 (2.17)	320 (2.15)	320 (2.15)
$HgBr_2$	206.5 (2.02)	209 (2.07)	209 (2.07)	—	209.5 (2.08)	207 (2.03)
HgI_2	149 (1.67)	—	151 (1.71)	—	151 (1.71)	153 (1.76)
$Hg(CN)_2$	—	—	—	415 (2.65)	411 (2.60)	—
	Dioxane	THF	DMF	DMSO	Pyridine	
$HgCl_2$	320 (2.15)	319.5 (2.14)	310 (2.02)	—	280 (1.64)	
$HgBr_2$	208 (2.05)	202 (1.93)	200 (1.89)	196 (1.82)	188 (1.67)	
HgI_2	154 (1.78)	148 (1.64)	145 (1.58)	142 (1.51)	140 (1.42)	

a) J. R. Ferraro, "Low-Frequency Vibrations of Inorganic and Coordination Compounds," Plenum, New York (1971), p. 142.

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* In the case of $Hg(CN)_2$, a Raman line due to $Hg-C\equiv N$ bending was observed at 270—272 cm^{-1} (in acetone, methanol, ethanol, dioxane and water) or at 267 cm^{-1} (in pyridine) and another due to $C\equiv N$ stretching at 2195—2200 cm^{-1} (in methanol and ethanol) or at 2180 cm^{-1} (in pyridine). Insolubility of this compound in many of the solvents used, and overlapping with the Raman lines of the solvents, hindered closer study of the solvent effect in this case.

** The methyl halides showed two Raman lines, *i. e.* the Hg–X and Hg–CH_3 stretching frequencies; the line corresponding to X–Hg–CH_3 bending could not be located with certainty, probably because of its poor intensity.

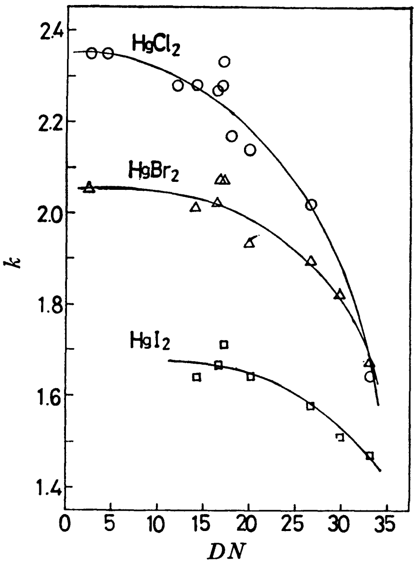

Fig. 1. *k vs. DN*.

TABLE 2. RAMAN FREQUENCIES OF $(CH_3)HgX$ AND APPARENT FORCE CONSTANTS OF Hg–X AND $Hg–CH_3$ BONDS

	Methanol	Pyridine	
$(CH_3)HgCl$	328(1.95)	316(1.81)	(Hg–Cl)
	554(2.52)	547(2.46)	$(Hg–CH_3)$
$(CH_3)HgBr$	225(1.75)	212(1.56)	(Hg–Br)
	546(2.45)	535(2.35)	$(Hg–CH_3)$
$(CH_3)HgI$	178(1.50)	175(1.57)	(Hg–I)
	535(2.35)	528(2.27)	$(Hg–CH_3)$

be seen that the effect of solvent change is remarkably smaller than in the case of the simple halides.

All these results can probably be understood if we assume that the molecules of the donor solvents used tend to assemble around the central mercury atom of the linear HgX_2 molecule and to form coordinate bonds with it. If this kind of intetaction is assumed to be chiefly electrostatic in nature, it is easy to see that $HgCl_2$, which contains the most ionic bonds and therefore the most positively charged mercury atom, is the most susceptible to it, and the accumulation of the negative ends of the solvent molecules around the mercury atom will substantially weaken the Hg–Cl bond. This kind of solvent effect will naturally increase with increasing Lewis basicity of the solvent and decrease in the order of $HgCl_2 > HgBr_2 > HgI_2$, and from simple halides to methyl halides which are expected to be more covalent in nature.

It is now of interest to note that decrease of *k* of HgCl in going from gas to pyridine solution is as large as 30—40%, being comparable with the change of *k* observed when a double bond is converted into a single bond. This means that strong solvation can weaken a chemical bond to such a great degree. This effect will probably be an important reason for the fact that the Hg–X bond energies in the gas molecules decrease in the order $HgCl_2$ (54 kcal/mol)→$HgBr_2$(44)→HgI_2(35),[4] while the ease of formation of these molecules in aqueous solution increases in the opposite way (heats of formation: $HgCl_2$ (−13 kcal/mol)→$HgBr_2$(−21)→HgI_2(−34)).

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References

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4) J. E. Huheey, "Inorganic Chemistry," Harper and Row, New York (1972), p. 698.

5) J. J. Christensen, *et al.*, "Handbook of Metal Ligand Heats", 2nd ed., Dekker, New York (1975).