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Molecular Complexes of Mercuric Halides with Aromatic Hydrocarbons: Electronic Spectra and Stability Constants

IDA MARIA VEZZOSI, GIORGIO PEYRONEL and ALINE F. ZANOLI
Istituto di Chimica Generale e Inorganica, University of Modena, 41100 Modena, Italy
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It has been demonstrated that mercuric halides form solid molecular complexes with aromatic hydrocarbons; the chloride complexes are less stable than those of bromide and iodide. A spectrophotometric study of the U.V.–Visible spectra of these complexes in dichloromethane solution shows that λ_{max} *and* ε_{max} *of the C.T. bands of the complexes are respectively longer and greater for the bromide than for the chloride complexes. Job's method shows that these complexes in solution have a 1:1* $HgX_2/Arene$ *ratio. The equilibrium constants* $K = [HgX_2 \cdot Arene]/[HgX_2] \cdot [Arene]$ *were determined by the Benesi–Hildebrand method. The equilibrium constants of the bromide complexes are always greater than those of the chloride complexes. The energy* $h\nu$ *of the charge transfer bands increases linearly with increasing ionization potentials of the aromatic hydrocarbons.*

Introduction

Mercuric halides easily form molecular complexes with *p*-dioxane, ketones and other molecules containing donor atoms such as O, N, S: some of these complexes have been isolated in the solid state and studied by several experimental techniques. The molecular complexes of these halides with the aromatic hydrocarbons, however, have not been extensively studied.

The molar solubilities in water, benzene and toluene, and the distribution coefficients of mercury(II) halides were studied by Marcus.[1] Dipole moments[2] and solubility[3] measurements led Eliezer to conclude that in donor solvents like benzene or dioxane (D) mercuric halides have a bent structure and form predominantly 2:1 solvent/solute complexes presumably with a distorted tetrahedral configuration HgX_2D_2. The far infrared spectra of mercuric halide solutions in benzene and other donor solvents also showed [4,5] a definite interaction between the solvent and mercury halides and suggested the existence in solution of tetrahedral or octahedral HgX_2–solvent complexes.

More recently, Eliezer *et al.*[6] studied the UV spectra of the mercuric halides in aromatic solvents by analogy with those of other charge-transfer complexes of the aromatic hydrocarbons. They postulated that, since all the complexes mentioned in this comparison are of the C.T. type and of 1:1 composition, it can be assumed that the mercuric halides interact with benzene forming a 1:1 C.T. complex.

Since, in the previous studies, uncertainty exists regarding the stoichiometry of these complexes in solution, and since no solid complexes have hitherto been isolated, we set out to determine the equilibrium constants of these compounds too using the same preparative and spectrophotometric methods as we had previously used on other aromatic molecular complexes.[7]

Experimental

All the reagents used for the preparations were of pure chemical grade. For the spectrophotometric measurements they were of spectroscopic grade or purified as follows: mercuric halides were recrystallized from dichloromethane or cyclohexane; the aromatic hydrocarbons (HAr) were purified by distillation or by chromatography on silica gel or neutral allumina and dehydrated by conventional methods; dichloromethane (DCM) was dehydrated on $CaCl_2$ and purified by fractional distillation; collecting the fraction which distillates at 40° C.

Solid complexes of mercuric halides with toluene and ethylbenzene were obtained by very slowly cooling a saturated solution (at 80° C) of the halide in the aromatic hydrocarbon. The solid complexes of mercuric chloride obtained with both these aromatic hydrocarbons rapidly lose the coordinated solvent molecules and could not be analysed. The toluene and ethylbenzene complexes of bromide and iodide, on the other hand, are very stable in air, slowly decomposed by hydrogen chloride and soluble in ethyl alcohol. The HgI_2 complexes with toluene and ethylbenzene turn from yellow to red in two days, apparently without losing their crystalline form.

TABLE I. Analytical data, found % and (calcd.%), for the solid HgX_2·Arene complexes.

Compound	Colour	HgX_2·	Ar	Diox.
$2HgBr_2$·Toluene	pearly-white	88.07(88.66)		
$2HgI_2$·Toluene	yellow	90.24(90.80)		
$2HgBr_2$·Ethylbenzene	ivory-yellow	87.39(87.27)		
$3HgI_2$·2Ethylbenzene	yellow	85.60(85.51)		
$HgBr_2$·Acenaphthene	white	69.63(70.04)	29.40(29.96)	
HgI_2·Pyrene	yellow	69.06(69.19)	30.90(30.81)	
HgI_2·Pyrene·Dioxane	white	60.69(61.02)	26.51(27.15)	12.80(11.83)
HgI_2·2Anthracene	yellow	56.25(56.04)	43.38(43.96)	

The complex $HgBr_2$·Acenaphthene was precipitated by adding isooctane to a solution of $HgBr_2$ in ethylether, saturated with acenaphthene. The complexes HgI_2·Pyrene and HgI_2·2Anthracene were precipitated by adding petroleum ether to a saturated solution of the aromatic hydrocarbon and HgI_2 in dioxane. The complex HgI_2·Pyrene·Dioxane was obtained by cooling a dioxane solution saturated at 80° C with HgI_2 and pyrene.

It was not possible with these preparative methods to obtain the mercuric chloride complexes of acenaphthene, pyrene and anthracene, or the mercuric bromide complexes of pyrene and anthracene. The instability of the toluene and ethylbenzene complexes of $HgCl_2$ and the impossibility to obtain its complexes with the other hydrocarbons indicate that the $HgCl_2$ complexes are less stable than the other complexes.

The toluene and ethylbenzene complexes were analysed by decomposing them with diluted hydrogen chloride and by precipitating and weighing mercury as HgS. The acenaphthene, pyrene and anthracene complexes were decomposed with water and the aromatic hydrocarbon was extracted with heptane and weighed after the evaporation of the solvent; mercury was gravimetrically determined as HgS in the aqueous solution. Analytical results are given in Table I.

Spectrophotometric measurements were performed with a Hilger Uvispek single beam spectrophotometer with highly sensitive galvanometric reading, mostly on dichlormethane solutions. $HgCl_2$ and $HgBr_2$ are very soluble in this solvent, which is highly transparent in the spectral region used for the measurements.

Results and Discussion

The mercuric halide: aromatic hydrocarbon ratio in the solid complexes chiefly depends on the electronic structure of the aromatic molecule and on its steric hindrance, and on the nature of the mercuric halide. As in other metal complexes with aromatic hydrocarbons,[7] coordination occurs through an interaction of the π electrons of some sites of the donor aromatic molecule with some empty orbitals of the mercury atom. Consequently, the linear geometry of the free molecule of the mercury halide should be bent, as was shown by the dipole moments[2] and the far infrared spectra[4,5] of their arene solutions.

The spectrophotometric measurements were performed only on the benzene and substituted benzene solutions, as not only do they have a simpler molecular structure, which presumably gives simpler complexes in solution, but they also afford an opportunity of comparing spectroscopic data in a homologous series differing only in the number and in the length of the aliphatic substituents. The use of dichloromethane solutions will be discussed later. HgI_2 could not be used for spectrophotometric measurements because in DCM solution it very soon gives free iodine, recognizable by the colour and the visible spectrum of the solution.

The electronic spectra of the dichlormethane solutions, containing a great excess of the aromatic hydrocarbon compared to their HgX_2 content, showed an increased absorbance in the region 260–300 nm in comparison with the solutions of the pure aromatic hydrocarbon at the same concentration. The difference curves obtained by substracting the spectrum of the hydrocarbon solution from that of the solution containing the hydrocarbon and the halide, distinctly show the charge transfer bands of the complexes; the λ_{max} of these bands and their ε_{max} referring to the HgX_2 concentration in the solution, are given in Table II.

The C.T. λ_{max} observed for these diluted DCM solutions differ from those given by Eliezer *et al.*[6] for the HgX_2 solutions in the pure aromatic hydrocarbons. A test on the $HgBr_2$ solution in benzene shows that the position of the C.T. maximum depends heavily on the $HgBr_2$ concentration in the pure arene (Figure 1A). Since the concentrations used are not given in the work of Eliezer *et al.*[6], a comparison of the two series of results in meaningless: only the C.T. λ_{max} of the *o*-xylene solutions are casually identical in both works.

The variability of the maxima positions depending on different concentrations of HgX_2 in the pure hydrocarbon may indicate that more than one complex is present in these solutions, probably in equilibrium

TABLE II. Charge transfer bands (λ_{max}, ε_{max}, hν) and equilibrium constants (K=[HAr·HgX_2]/[HAr][HgX_2], at room temperature, for the 1:1 complexes of the mercuric halides with aromatic hydrocarbons (HAr) in dichloromethane (DCM) solutions. I.P. = ionization potential (e.v.) of HAr.[15]

DCM	$HgCl_2$				$HgBr_2$				I.P.
	λ_{max} nm	ε_{max}	hν (ev)	K	λ_{max} nm	ε_{max}	hν (ev)	K (mol^{-1} l)	
Benzene	267.3	71	4.636	0.200	270.2	105	4.587	0.301	9.25
Toluene	274.5	114	4.515	0.278	275.8	143	4.494	0.367	8.82
Ethylbenzene	274.0	130	4.524		276.8	124	4.475		8.77
s-Buthylbenzene	–	–	–		274.0	141	4.524		8.68
o-Xylene	275.2	152	4.500	0.327	279.1	211	4.441	0.421	8.52
*m*Xylene	280.0	186	4.426		280.5	193	4.419		8.56
p-Xylene	281.5	145	4.400		283.0	157	4.370		8.45
Mesitylene	282.0	215	4.395	0.428	283.5	275	4.372	0.538	8.40

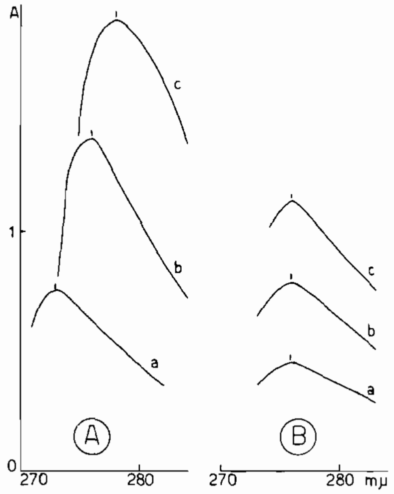

Figure 1. A) Electronic spectra of the solutions of $HgBr_2$ in benzene at concentrations: a) $0.48 \times 10^{-2} M$, $\lambda_{max} = 273.0$ nm; b) $0.96 \times 10^{-2} M$, $\lambda_{max} = 276.0$ nm; c) $1.91 \times 10^{-2} M$, $\lambda_{max} = 278.0$ nm. B) Electronic spectra of the DCM solutions of $HgBr_2$ at constant concentration $1.9 \times 10^{-2} M$ and of toluene at concentrations: a) 0.28 *M*, b) 0.56 *M*, c) 0.84 *M*. Constant $\lambda_{max} = 275.8$ nm for the three curves.

to one another. The use of dilute solutions of both reagents (halide and arene) in a less active solvent like DCM, in which mercuric halides do not absorb at all in the spectral region used for this study, seems to enable the first step reaction: $HgX_2 + HAr \rightleftharpoons HgX_2 \cdot HAr$ to be observed and the true spectrum of its 1:1 C.T. complex to be identified. Figure 1B shows that in DCM the position of the C.T. maximum for the $HgBr_2$·Toluene complex is constant for a constant [$HgBr_2$] in a wide range of arene concentration (0.28 to 0.84 m/l). The C.T. maximum stays constant even when the concentration of HgX_2 is changed from 0.9 to 1.8×10^{-2} *M*, with constant arene concentration.

Using Job's method of continuous variations, the mercuric halide: aromatic hydrocarbon ratio in the DCM solutions was clearly defined as 1:1 for several systems (Figure 2A).

Applying the Benesi–Hildebrand method[8], the equilibrium constants K = [HgX_2·HAr]/[HgX_2] [HAr] of the complexes in DCM solutions of a large excess of arene with respect to HgX_2 were obtained at 20° C from the plots of [HgX_2] l/A (l = cell width, A = absorbance) versus 1/[HAr] for different wave lengths in the region of the C.T. maximum. All the plots gave straight lines with positive intercepts (Figure

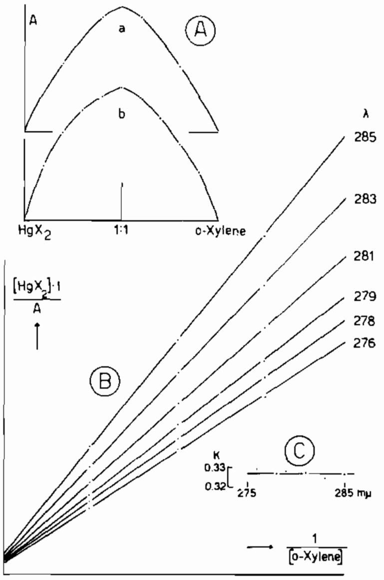

Figure 2. A) Job's diagrams for the DCM solutions of a) *o*-xylene + $HgCl_2$, total concentration $1.7 \times 10^{-2} M$, $\lambda = 274$ nm; b) *o*-xylene + $HgBr_2$, total concentration $1.8 \times 10^{-2} M$, $\lambda = 286$ nm. B) Benesi–Hildebrand plot for the DCM solutions of $HgCl_2$ at constant concentration $1.084 \times 10^{-2} M$ and of *o*-xyiene at concentrations 0.560, 0.280, 0.187 *M*, for different wavelengths. C) Plot of the equilibrium constant K versus λ.

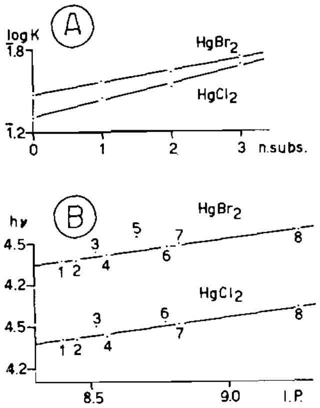

Figure 3. A) Plot of logK versus the number of alkyl substituent in the aromatic ring. B) Plot of hν (e.v.) versus the ionization potential (e.v.) of the aromatic hydrocarbons: 1) mesitylene, 2) *p*-xylene, 3) *o*-xylene, 4) *m*-xylene, 5) buthylbenzene, 6) ethylbenzene, 7) toluene, 8) benzene.

2B), indicating that the B–H method can reasonably be applied.[9, 10]

The good constancy of the K values over a wide range of wave lengths (Figure 2C) indicates that the stability constants are reliable and correspond to a 1 : 1 complex in solution[11], as is confirmed by the results of Job's method. Log K of the two series of complexes increases in almost linear relationship to the number of substituents in the benzene ring (Figure 3A).[12]

All the stability constants of the $HgBr_2$ complexes are significantly greater than those of the corresponding $HgCl_2$ complexes. This result does not agree with the conclusions postulated by Eliezer *et al.*[6], namely that their equilibrium constants follow the order $K\,HgCl_2 > K\,HgBr_2 > K\,HgI_2$.

It is generally admitted[12] that an increase in the strength of interaction in a C.T. complex is accompanied by a shift of the λ_{max} of the complex to longer wavelength, and that the more stable the complex becomes, the greater the ε_{max} are.[13] Both these conditions are fulfilled in this case, the $HgBr_2$ complex showing for the same arene longer λ_{max} and greater ε_{max} values than the $HgCl_2$ complex, in agreement with the trend in their equilibrium constants.

This is remarkable because in benzene solution the dipole moment is greater for $HgCl_2$ than for $HgBr_2$.[2] A similar behaviour was observed for the pyrene complexes of antimony trihalides,[7] the 1 : 1 C.T. complex of the less polar $SbBr_3$ having a greater equilibrium constant in DCM solution than the 1 : 1 C.T. complex of the more polar $SbCl_3$.

This behaviour could be explained by admitting, as in the case of the antimony halides,[7] that since bromine is a better acceptor than the chloride atom[12] it could take part in the mercury halide–arene complex formation with a bromine–arene interaction accompanying the normal mercury–arene interaction. A "short" intermolecular contact between the pyrene molecule and a bromine atom of the $SbBr_3$ molecule was observed in the crystal structure of the $2SbBr_3 \cdot$Pyrene complex[14] and could support this view. For both series of complexes, the energy (hν) of the charge transfer bands increases in linear relationship to the ionization potentials (I.P. in e.v.) of the aromatic hydrocarbon (Table II and Figure 3B).[6, 15]

Acknowledgments

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