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The Uncharged Mixed Halides of Mercury(II). Equilibrium Constants and Ultraviolet Spectra[1]

BY THOMAS G. SPIRO AND DAVID N. HUME

A general method is given for the study of the mixed complex formation equilibrium, $MA_2 + MB_2 = 2 MAB$, and is applied to spectrophotometry. A spectrophotometric study of the uncharged mixed mercuric halides at 25° in a $10^{-3} M$ perchloric acid medium gave the following equilibrium constants (log units) for the above reaction: 1.07 ± 0.08, 1.35 ± 0.17, and 1.14 ± 0.11 for $HgBrI$, $HgClI$ and $HgClBr$, respectively. These results are compared with those of a previous solvent extraction study of the same systems, and the stability in excess of that predicted statistically ($\log K = 0.60$) for all three mixed complexes is rationalized on the basis of polar interactions. The ultraviolet spectra of the complexes are also discussed.

The simplest case of mixed ligand complex formation occurs when a pair of binary ("mono-ligand") complexes exhibiting a coördination level of two react to form a single mixed complex. The "coördination level" of a complex is defined as the total number of coördination sites occupied by ligands other than solvent molecules. If neither of the parent complexes undergoes dissociation or disproportionation to an appreciable extent, then the only reaction occurring in solution will, in general, be of the type

$$MA_2 + MB_2 = 2MAB$$

where M is the common central group, and A and B are the two ligands. Marcus[2] has used this reaction to study the uncharged mixed mercuric halides by a solvent extraction technique. The same reaction can also describe mixed complex formation at the coördination level of four if the ligands are bidentate. Such mixed systems have been studied spectrophotometrically by Watters and co-workers for copper–pyrophosphate–ethylenediamine[3] and copper–ethylenediamine–oxalate[4] and by Bennett for copper–ethylenediamine–iminodiacetate.[5] A general method for the investigation of this reaction

is presented herein, and its application is illustrated with a spectrophotometric study of the uncharged mercury (II) halides.

Method.—Most methods of treating equilibrium data on complex systems use ligand and central group concentrations as experimental variables. For the reaction under consideration, however, the species M, A and B do not appear explicitly, and indeed their concentrations are assumed to be negligible. It is logical to use as variables the concentrations of the complexes of coördination level two which do appear explicitly in the reaction, or some functions thereof. Two variables are sufficient to determine the concentrations of all the relevant species, and the two chosen for the present method are the fraction of central group present as the mixed complex, MAB, and the ratio of the formal concentrations of the binary complexes. The following symbols will be used

C_{MA_2} = the formal concentration of MA_2, assuming no reaction

C_{MB_2} = the formal concentration of MB_2, assuming no reaction

$R = C_{MB_2}/C_{MA_2}$

C_M = the total concentration of central group present in all species

$\alpha_{11} = (MAB)/C_M$, the fraction of central group present as MAB

$K = (MAB)^2/(MA_2)(MB_2)$, the equilibrium constant for the reaction

(1) Taken in part from the Doctoral Dissertation of Thomas G. Spiro, Massachusetts Institute of Technology, July, 1960.

(2) Y. Marcus, *Acta Chem. Scand.*, **11**, 610 (1957).

(3) J. I. Watters and E. D. Loughran, *J. Am. Chem. Soc.*, **75**, 4819 (1953).

(4) R. DeWitt and J. I. Watters, *ibid.*, **76**, 3810 (1954).

(5) W. E. Bennett, *ibid.*, **79**, 1291 (1957).

From the stoichiometry of the reaction and from the law of mass action, it can be shown that

$$K = \frac{4\alpha_{11}^2}{(1 - \alpha_{11})^2 - (1 - R/1 + R)^2} \quad (1)$$

Equation 1 is quadratic in α_{11}, and can be reduced with the quadratic formula to

$$\alpha_{11} = \frac{1 \pm \sqrt{1 - \frac{4R}{(1 + R)^2}(1 - 4K^{-1})}}{(1 - 4K^{-1})} \quad (2)$$

Since α_{11} is, of necessity, less than unity, only the root with the minus sign before the radical is real.

Equation 2 gives the theoretical distribution of α_{11} as a function of R, at any given value of K. From it a family of curves can be constructed for a series of values of K. (For convenience, log R is used instead of R, since the resulting curves are symmetric with respect to log $R = 0$.) If α_{11} can be measured experimentally as a function of R, then the experimental points can be plotted and compared with the theoretical distribution. Such comparison should give at once (1) an approximate value for the equilibrium constant, (2) an estimate of the scatter of the points, (3) the goodness of fit of the data, from which one can detect systematic experimental errors or failures of the original assumption that dissociation or disproportionation is negligible. From equation 1, K can be calculated for each point in which one has confidence.

Discussion of Error.—There are two principal sources of error in the above procedure. One is the uncertainty in the determination of α_{11}, which depends on the particular experimental technique used and which is increased in the subsequent calculation of K. Differentiation of equation 2 with respect to α_{11} at the point $R = 1$ (where the highest accuracy in determining K is to be expected), gives

$$dK/K = (K^{1/2} + 2)d\alpha_{11}/\alpha_{11}$$

which means that a small relative error in the determination of α_{11} is magnified by a factor of $(K^{1/2} + 2)$ in calculating K, even at the point of greatest accuracy. Clearly, the determination of large constants involves a considerable inherent uncertainty on theoretical grounds alone. This is a reflection of the fact that, as Marcus has pointed out,[2] the distribution of complexes in this system is not a sensitive function of the equilibrium constant, if the latter is "large."

The other possibly serious source of error is the assumption that $MA_2 + MB_2 = 2 MAB$ is the only reaction taking place to a significant extent. Both the dissociation and disproportionation of the parent complexes must be negligible. For monodentate ligands, this condition probably restricts the method to complexes of mercury(II) and silver-(I). A wider choice may be afforded, however, for bi- and tridentate ligands. One can estimate in advance the extent of the side-reactions if stepwise formation constants for the binary complexes are known.

Determination of α_{11} by Spectrophotometry.—A variety of experimental methods may, in principle, be applied to the determination of the extent of mixed complex formation. Marcus has illustrated the use of solvent extraction,[2] a technique which depends on the distribution coefficients of the individual complexes. (He did not, however, calculate values of α_{11} but determined K directly from distribution data.) If any or all of the species absorb light in an accessible spectral range, spectrophotometry may be used to investigate the reaction. To do so, one relies on Beer's law, which, for the system under consideration, may be written

$$A = \epsilon_{20}(MA_2) + \epsilon_{11}(MAB) + \epsilon_{02}(MB_2) \quad (3)$$

A is the solution absorbance, corrected to 1.0 cm. solution thickness, and ϵ_{20}, ϵ_{11} and ϵ_{02} are the molar absorptivities of MA_2, MAB and MB_2, respectively. From stoichiometry and equation 3 it can be shown that

$$\alpha_{11} = \Delta A/\Delta\epsilon \ C_M \quad (4)$$

where

$$\Delta A = A - (\epsilon_{20}C_{MA_2} + \epsilon_{02}C_{MB_2})$$

and

$$\Delta\epsilon = \epsilon_{11} - \frac{1}{2}(\epsilon_{20} + \epsilon_{02})$$

Obviously, if the absorptivity of the mixed complex is the same as the mean absorptivity of the parent complexes, $\Delta\epsilon = 0$, and there is no spectrophotometric evidence of mixed complex formation. On the other hand, the greater the value of $\Delta\epsilon$ that can be obtained relative to the total molar absorbance, the greater will be the sensitivity of the measurements. Therefore, the study should be carried out at those wave lengths where $\Delta\epsilon$ is maximal.

In equation 4, C_{MA_2} and C_{MB_2} are known, and ϵ_{20} and ϵ_{02} can be measured independently from Beer's law plots of the binary complexes while ϵ_{11} can be determined from mixtures having low or high values of R. In either range, one of the parent complexes is present in large excess, and the other is converted essentially quantitatively to the mixed complex. The result is a two-component mixture, for which the single unknown, α_{11}, can be determined straightforwardly. To this end, the expressions

$$A - \epsilon_{20}C_{MA_2} = (2\epsilon_{11} - \epsilon_{20})C_{MB_2} \text{ (for low } R\text{)}$$

and

$$A - \epsilon_{02}C_{MB_2} = (2\epsilon_{11} - \epsilon_{02})C_{MA_2} \text{ (for high } R\text{)}$$

can be derived. For the two cases, plots of the left side against C_{MB_2} and C_{MA_2}, respectively, should produce straight lines passing through the origin, from whose slopes ϵ_{11} can be calculated. As R approaches unity, the solutions change from essentially two-component to three-component systems, and the above plots will deviate from linearity (provided $\Delta\epsilon \neq 0$). This deviation is in itself a proof of mixed complex formation since, if none occurs, the solutions always contain two components, and the plots should be linear over the entire concentration range.

The present method for studying the reaction $MA_2 + MB_2 = 2MAB$, using spectrophotometry, may now be summarized. First, the spectra of MA_2 and MB_2, and also of MAB, are determined using linear plots in regions of low or high R. Then, wave lengths are selected where $\Delta\epsilon$ is maximal, and from absorbance data α_{11} is measured in the region where R is approximately unity. The values are plotted as a function of log R and com-
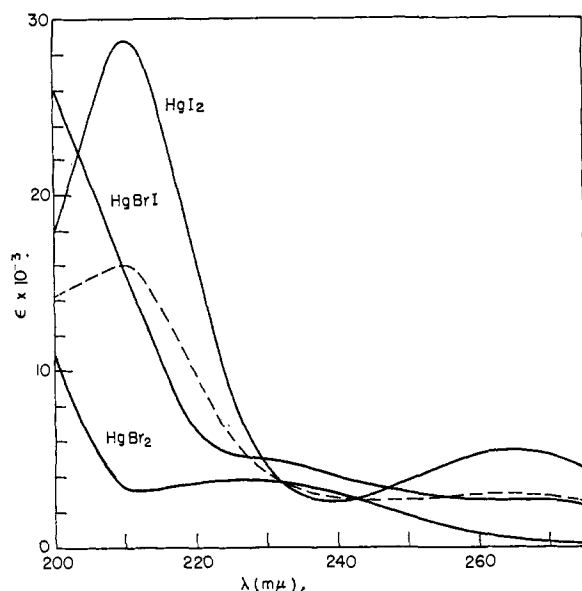
Fig. 1.—Spectra of HgI₂, HgBr₂ and HgBrI. The dashed curve is the median line: $\frac{1}{2}(\epsilon_{20} + \epsilon_{02})$.

pared with the theoretical distribution. Finally, for reliable data, K is calculated point by point and averaged.

The Mixed Mercuric Halides.—The formation of HgClBr, HgClI and HgBrI from the binary mercuric halides serves as a good illustration of the applicability of the method outlined above. From formation constants determined by Sillén and co-workers[6] and by Marcus,[7] it can be shown that the extent of disproportionation is negligible for all three binary complexes. The extent of dissociation may also be neglected unless the concentrations are very low, a point which will be considered in detail later. Marcus[2] studied the same systems by measuring the distribution of radiomercury between water and benzene.

Experimental

Triply distilled water was used throughout. Stock solutions of mercuric chloride and mercuric bromide were prepared directly by dissolving accurately weighed amounts of the analytical reagents (Mallinckrodt). The mercuric iodide (Baker reagent) was partially recrystallized from ethanol and washed repeatedly with distilled water, since the untreated material showed evidence of a small amount of an ultraviolet absorbing impurity. The low solubility of mercuric iodide prevented direct preparation of a stock solution. Instead, an excess was shaken in water for several hours and the essentially saturated solution was filtered through sintered glass. A portion was made up to 0.2 M in sodium iodide and the mercury content determined spectrophotometrically. At this iodide concentration, the mercury is converted quantitatively to the tetraiodomercurate ion, which has an absorption peak at 323 mμ. The peak absorptivity was determined by dissolving weighed samples of mercuric chloride and iodide directly in 0.2 M NaI. The concentrations of the mercuric chloride and bromide stock solutions were also checked by this method. The estimated uncertainty in the concentrations of all solutions was less than 1%. For the HgClI and the HgBrI studies, the total concentration of mercury was kept at about 0.05 mM, while for the HgClBr study it was about 0.4 mM. All stock solutions were adjusted to pH 3.0 with perchloric acid to prevent any hydrolysis of the complexes. No inert electrolyte was added and, consequently, the ionic strength was 10⁻³ M in all cases.

(6) L. G. Sillén, Acta Chem. Scand., 3, 539 (1949).
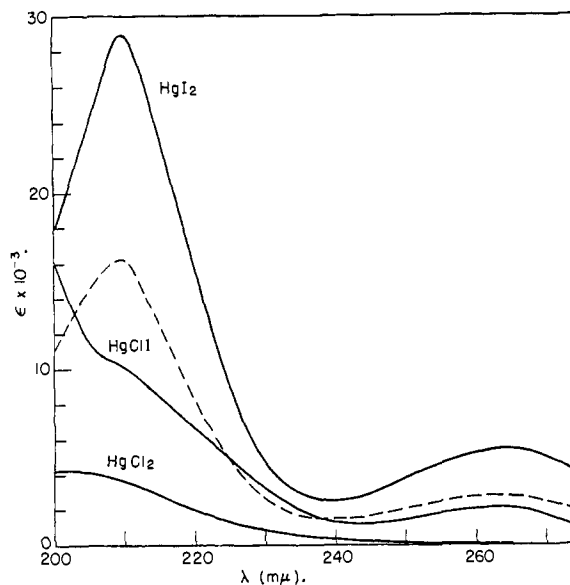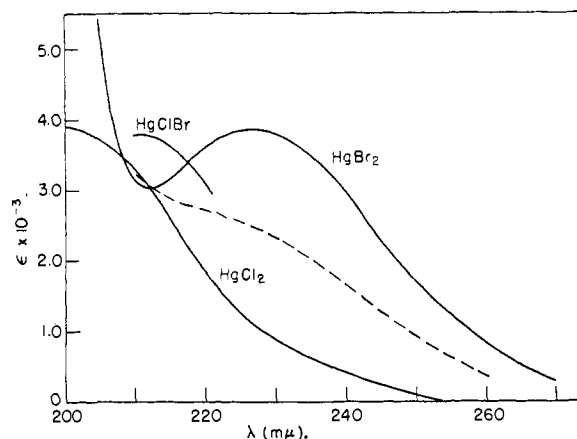(7) Y. Marcus, ibid., 11, 329 (1957).

Fig. 2.—Spectra of HgI₂, HgCl₂ and HgClI.

Fig. 3.—Spectra of HgBr₂, HgCl₂ and HgBrCl.

Preliminary measurements were recorded on a Cary Model 11 spectrophotometer, while final measurements were taken with a Beckman DU spectrophotometer equipped with a photomultiplier. The cell compartment temperature of the DU was kept constant with a circulating water-bath thermostated at 25.0 ± 0.01°. All solutions were also thermostated prior to measurement with the Beckman instrument.

Absorptivities.—Spectra of the complexes were determined from measurements recorded on the Cary spectrophotometer. Absorptivities of the mixed complexes were calculated at frequent wave length intervals from linear plots of $A - \epsilon_{20}C_{MA_2}$ against C_{MB_2} at low R and of $A - \epsilon_{02}C_{MB_2}$ at high R. The resulting spectra are shown in Figs. 1, 2 and 3. For each system, the absorptivities were re-determined in the regions of maximum $\Delta\epsilon$, using the Beckman spectrophotometer. ϵ_{20} and ϵ_{02} were calculated as the slopes of absorbance *versus* concentration plots for the binary complexes, while ϵ_{11} was determined from linear plots in ranges of low and high R, as above. The results are shown in Table I.

Equilibrium Constants.—Values of α_{11} ($= \Delta A/\Delta\epsilon C_M$) were calculated for each point in the vicinity of R equal to unity and plotted against log R. The resulting distributions were compared with the theoretical curves as shown in Figs. 4, 5 and 6. Finally, K was calculated for each point, and log K was averaged for all points in each system (Table II). (The only points omitted were those at the lowest value of R in the HgClI system, which lie very close to $K = \infty$.)

Discussion

Equilibria.—A close examination of the measured distributions (Figs. 4, 5 and 6) sheds light on

Table I

Absorptivities of the Complexes

	λ (mμ)	ϵ_{20} ($\times$ 10^{-3})	ϵ_{02} ($\times$ 10^{-3})	ϵ_{11}($\times$ 10^{-3})	$\Delta\epsilon$ ($\times$ 10^{-3})
	219	3.52 $\pm$ 0.001	16.66 $\pm$ 0.03	5.61 $\pm$ 0.03	-4.48 $\pm$ 0.03
HgBr$_2$	220	3.60 $\pm$ .01	15.02 $\pm$ .06	5.29 $\pm$ .06	-4.02 $\pm$ .06
HgI$_2$^{a}	221	3.65 $\pm$ .01	13.43 $\pm$ .05	5.02 $\pm$ .05	-3.53 $\pm$ .05
	209	3.54 $\pm$ .01	26.92 $\pm$ .13	9.12 $\pm$ .15	-6.11 $\pm$ .15
HgCl$_2$	210	3.41 $\pm$ .01	27.06 $\pm$ .11	8.95 $\pm$ .11	-6.29 $\pm$ .11
HgI$_2$^{a}	211	3.30 $\pm$ .01	26.76 $\pm$ .09	8.87 $\pm$ .09	-6.16 $\pm$ .09
	212	3.05 $\pm$ .02	3.06 $\pm$ .02	3.76 $\pm$ .03	0.70 $\pm$ .03
HgCl$_2$	213	2.92 $\pm$ .02	3.07 $\pm$ .01	3.75 $\pm$ .02	.76 $\pm$ .02
HgBr$_2$^{a}	215	2.59 $\pm$ .01	3.16 $\pm$ .01	3.60 $\pm$ .01	.72 $\pm$ .01

^{a} The first complex of each pair is taken as MA$_2$.

the validity of the data. Clearly there is a fair amount of scatter in the points, both between different wave lengths and between solutions. This is a reflection of inaccuracies in the measurements aggravated by the small relative values of $\Delta\epsilon$ which were obtainable. The scatter is magnified in calculating the equilibrium constants, as was pointed out in the error discussion above. An examination of estimated uncertainties in the results (Table II) indicates that the spectrophotometric method gives better precision than the solvent extraction method used previously
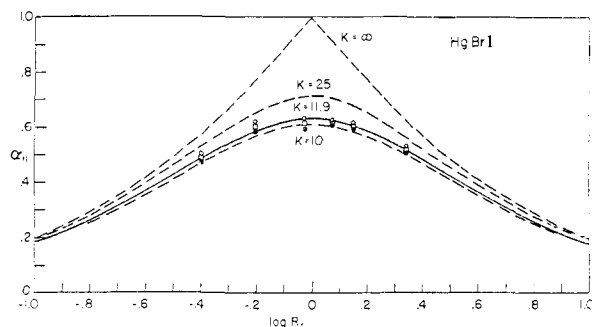
Table II

Equilibrium Constants

	Log K	
	This work	Marcus[9]
HgBrI	1.07 $\pm$ 0.08	1.10 $\pm$ 0.20
HgClI	1.35 $\pm$ .17	1.75 $\pm$ .20
HgClBr	1.14 $\pm$ .11	2.0 $\pm$ .5

Repeated analyses failed to show any discrepancy in the concentrations of the stock solution. The difficulty appears more likely to be a failure of the original assumption that dissociation of the complexes is negligible. From the formation constants of Sillén[8] and Marcus[7] it can be shown

Fig. 4.—Distribution of HgBrI: ●, 219 mμ; □, 220 mμ; O, 221 mμ.
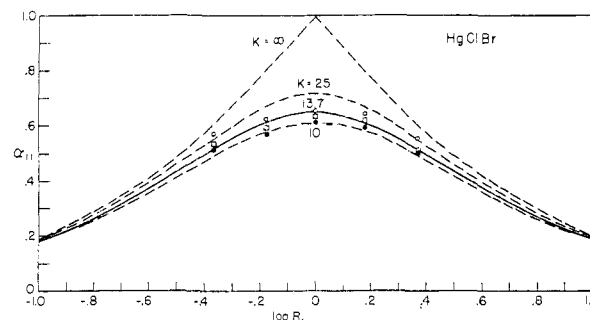
Fig. 6.—Distribution of HgBrCl: □, 212 mμ; ●, 213 mμ; O, 215 mμ.

that, at the concentrations used in these solutions, $C_M \simeq 10^{-4.3}$ M, the extent of dissociation is less than 0.1% for mercuric iodide and only about 1% for mercuric bromide. For mercuric chloride it is about 10%, which means that the actual values of R are about 10% higher in the HgClI system than were calculated, a factor which adequately accounts for the observed shift in the distribution. As a result, the calculated value of K is probably somewhat low. For the HgClBr system C_M was raised to $10^{-3.4}$, at which value the calculated extent of dissociation of mercuric chloride decreases to about 3% and scarcely affects the distribution of HgClBr.[8]

In order to compare the present results with those of Marcus in 0.5 M sodium perchlorate, it is first necessary to estimate the effect of ionic strength on the equilibria. Marcus[9] measured the activity
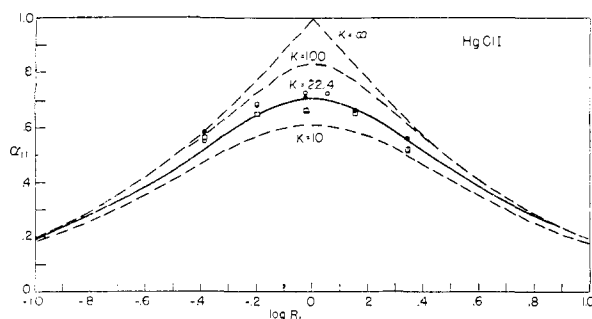

Fig. 5.—Distribution of HgClI. The symbols represent three independent runs. Values at the three wave lengths used, 209, 210 and 211 mμ, are averaged for each point.

The distribution of HgClI (Fig. 5) is somewhat anomalous in that values at low R appear to be too large, and those at high R appear to be too small. The points represent averages for the three wave lengths used and are taken from three separate sets of solutions, so the effect is definitely reproducible. The data would fit the theoretical distribution if the actual values of R were greater than the calculated values by a small constant factor.

(8) The formation constants of Sillén and Marcus were measured in 0.5 M sodium perchlorate medium and therefore are not strictly applicable to these solutions. One would expect the extent of dissociation to decrease somewhat at lower ionic strengths. Nevertheless, the order of magnitude of the effect should be the same.

(9) Y. Marcus, Acta Chem. Scand., 11, 329 (1957).

coefficients of the mercury(II) halides as a function of ionic strength in sodium perchlorate solutions and found that, below an ionic strength of 1.5 M, the relation could be expressed by a salting out coefficient of 0.14 for all three halides. Consequently, in 0.5 M sodium perchlorate the activity coefficients of the binary halides should be 1.1. [The salting out (or in) coefficient is a complex function of the nature of both the electrolyte and the non-electrolyte.. For a given electrolyte and chemically similar non-electrolytes with nearly the same molecular dimensions, the salting out coefficient appears to decrease with increasing dipole moment of the neutral molecules.[10]] The uncharged halides of mercury are presumably linear.[6,11] The mixed ligand complexes, therefore, have a net dipole moment, absent in the parent compounds.

It can be assumed therefore that the activity coefficient increases less for the mixed complexes than for the parent binary complexes as the ionic strength is increased. Consequently, the stoichiometric equilibrium constant, $K = (MAB)^2/(MA_2)(MB_2)$, should increase with increasing ionic strength. The effect, however, should not be large. If we assume that the activity coefficient of MAB does not increase at all, then the equilibrium constant in 0.5 M sodium perchlorate will be 30% or 0.11 log unit greater than at zero ionic strength, a discrepancy which is of the same order of magnitude as the uncertainty in the experimental determinations of K.

Table II shows that the two log K values for HgBrI are in very good agreement. On the other hand, there is a significant discrepancy between the log K values for HgClI and an even larger one for HgClBr. Although they are in the right direction, the discrepancies seem too large to be accounted for on the basis of ionic strength differences. The error involved in the present determination of the HgClI system already has been discussed, and it should be pointed out that the same criticism applies to Marcus' work. He reports a total mercury concentration between 10^{-4} and 10^{-5} M in all cases, a range in which the extent of dissociation of mercuric chloride is significant. Since, in the present study, this error was largely corrected in the HgClBr system by increasing the total concentration, somewhat greater confidence can be attached to the present value of log K for this system.

These differences notwithstanding, it is quite clear, as Marcus has also concluded, that the constants are significantly greater than the statistically expected constant, $K = 4$ (log $K = 0.60$). Professor E. L. King[12] has made the reasonable suggestion that the extra stabilization may be the result of polar effects. One would expect a medium, such as water, to stabilize the polar mixed ligand complexes relative to the non-polar binary complexes. This line of reasoning is supported by the observation of Marcus[2] that the constants in benzene are smaller than those in the aqueous

phase. On this basis, the pattern of constants found in the present investigation—essentially equal for HgBrI and HgClBr, which should have comparable dipole moments, and larger for HgClI, which should have the largest dipole moment—is somewhat closer to expectation than that reported by Marcus.

Spectra.—Although this investigation was concerned primarily with the equilibria of mixed complex formation, the spectra, determined in the course of the work, themselves deserve comment. The present results are in agreement with the findings of Fromherz and Lih[13] who observed intense peaks (log $\epsilon \simeq 3.7$) at 200 mμ for mercury(II) chloride, 226 mμ for the bromide and 265 mμ for the iodide. Their data show a rise in the mercuric iodide spectrum at lower wave lengths but do not extend far enough to show the very intense peak observed at 210 mμ in this study. The transitions are presumably of the charge transfer variety. The requirements for such transitions—intense absorption ($\epsilon \simeq 10^4$) in the ultraviolet region—are met in all cases. Convincing evidence for charge transfer mechanisms in the case of halides is provided by the frequently observed separation of two peaks in the spectra, corresponding satisfactorily with the frequency differences between the $2p_{1/2}$ and $2p_{3/2}$ states of the halogen atoms (7600, 3700 and 880 cm.$^{-1}$ for iodine, bromine and chlorine, respectively.)[14-16] The frequency difference for chlorine is apparently too small to be observed in most cases. For mercuric iodide two peaks are observed, at 210 and 265 mμ, with a frequency difference of 9870 cm.$^{-1}$, which is of the same order of magnitude as the theoretical separation. The second peak for mercuric bromide occurs below 200 mμ, the limit of the present measurements, but it appears that the separation is less for the bromide than for the iodide.

In the stepwise formation of metal halide complexes, it is frequently observed that the charge transfer peak shifts to longer wave lengths with successive substitution of halide in the coördination sphere of the metal. Rabinowitch[14] has suggested that this effect might be due to transfer of an electron from the anion shell as a whole, rather than from a definite anion. On this reasoning, one would expect that mixed halide complexes should give charge transfer peaks at frequencies intermediate between those of the parent complexes. This effect has, in fact, been observed for the mixed bismuth–chloride–bromide system, studied by Newman and Hume.[17] For the mixed mercuric halides one would expect, on this basis, that their spectra would show the same peaks as the parent complexes, shifted to intermediate frequencies. On the other hand, if the transitions were localized to a definite anion (a reasonable hypothesis in the case of the mercuric halides, in which the ligands are presumably on opposite sides of the central atom), one would expect mixed complex absorption to occur

(10) F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).

(11) C. L. Van Panthaleon Van Eck, H. B. M. Wolters and W. J. M. Jaspers, *Rec. trav. chim.*, **75**, 802 (1956).

(12) E. L. King, private communication.

(13) H. Fromherz and K. Lih, *Z. physik. Chem.*, **167**, 103 (1933).

(14) E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942).

(15) L. E. Orgel, *Quart. Revs.*, **8**, 422 (1954).

(16) L. I. Katzin, *J. Chem. Phys.*, **23**, 2055 (1955).

(17) L. Newman and D. N. Hume, *J. Am. Chem. Soc.*, **79**, 4581 (1957).

at the same wave lengths as for the binary complexes, but with intermediate intensity, i.e., the mixed complex spectra would be expected to follow the median lines shown in Figs. 3, 4 and 5.

A glance at the actual mixed complex spectra shows that neither hypothesis adequately explains the data. The intense peak of mercuric iodide at 210 mμ is indeed shifted to shorter wave lengths (inaccessible to the present measurements) for HgClI and HgBrI, implying interaction of the ligands for this peak. On the other hand, HgClI has a peak at 265 mμ, whose intensity is slightly less than half that of mercuric iodide. Therefore, the 265 mμ peak seems characteristic of iodide alone. The species HgBrI also absorbs at 265 mμ with an

intensity close to the median line, but, in addition, it shows some enhancement of absorption in the 230–250 mμ region which might be due to interaction of the ligands. A peak intermediate between those of mercuric chloride and mercuric bromide appears for HgClBr, but the overlap of the absorption bands is large, and the spectrum has been measured only in the region of maximum $\Delta\epsilon$ so that the interaction of the ligands is difficult to assess.

The Preparation and Some Properties of Platinum Hexafluoride[1,2]

BY BERNARD WEINSTOCK,[3] JOHN G. MALM AND E. EUGENE WEAVER[4]

Platinum hexafluoride is the first simple hexavalent platinum compound that has been prepared. This was achieved by burning a platinum wire in a fluorine atmosphere adjacent to a cold surface with yields of up to 70%. The formula has been established by chemical analyses and vapor density. A solid transition occurs at 3.0°, 32.5 mm. pressure and the fusion point is 61.3°, 586 mm. The heat of transition is 2140 cal. mole^{-1} and the heat of fusion is 1080 cal. mole^{-1}. The vapor pressure equations are: orthorhombic solid, $\log P$ (mm.) $= -3147.6/T - 6.09 \log T + 27.7758$; cubic solid, $\log P$ (mm.) $= 2528.7/T - 4.080 \log T + 20.6280$; liquid, $\log P$ (mm.) $= -5685.8/T - 27.485 \log T + 89.14962$. The boiling point is 69.14°, which is the highest boiling point of the known hexafluorides. The heat of vaporization at the boiling point is 7060 cal. mole^{-1}. The liquid density is 3.826 g. cc.$^{-1}$ at 64.3°. The density of the low temperature solid varies between 6.0–5.0 g. cc.$^{-1}$ in the range 77–254°K. The vapor and liquid are red in color and the solids appear black. The molecule does not rotate freely in any of the condensed phases. Platinum hexafluoride is the least stable and most reactive of the known hexafluorides. The use of PtF$_6$ as a fluorinating agent at room temperature to form BrF$_5$, NpF$_6$ and PuF$_6$ is described.

Introduction

Platinum hexafluoride represents the first hexavalent compound of platinum that has been formed with a monovalent element and definitely establishes the valence of six for platinum. Other hexavalent compounds of platinum have been previously reported but in all cases involve a polyvalent element. These compounds include the trioxide,[5] triselenide,[6] diphosphide[7] and diarsenide.[8] Owing to the multiple valency of the anion involved, it has been suggested that the valence of platinum in these compounds might be lower than the formula implies.[9] However, the synthesis of PtF$_6$ removes any question as to the existence of a hexavalent state for platinum.

The initial preparation and identification of PtF$_6$ has been reported.[10] This synthesis completed the 5d transition series of hexafluorides that had already included WF$_6$, ReF$_6$, OsF$_6$ and IrF$_6$. The

present paper describes the original work in more detail as well as some subsequent studies that have been made with PtF$_6$.

Experimental

Materials.—Platinum metal wire obtained from the Baker Platinum Division of Engelhard Industries was used in the preparations. Within the limits of spectrographic analysis this material was found to be free of impurities. The fluorine gas used in the syntheses was obtained from the Pennsalt Chemicals Corporation. Its analysis showed greater than 99% fluorine by volume. The fluorine contained a small amount of hydrogen fluoride which was removed by condensation with liquid nitrogen.

Preparation.—The apparatus previously described[10] that was used for the first preparation of platinum hexafluoride is shown schematically in Fig. 1. This reactor was constructed chiefly of Pyrex glass and contained 10 g. of 0.030 inch diameter platinum wire in the form of a spiral filament that was attached to electrically insulated nickel leads that were brought out of the apparatus through a Stupakoff seal. The filament was located directly below the surface of a spherical well which was kept full of liquid nitrogen during the course of the reaction.

Prior to admitting fluorine the system was evacuated to a pressure of about 10^{-6} mm. and was flamed while pumping to remove absorbed water. During the reaction a reservoir of liquid fluorine at the temperature of boiling nitrogen served to keep the fluorine pressure constant at about 300 mm. An electric current was passed through the platinum wire to initiate the reaction which then continued without external heating until the platinum was substantially consumed. The heat produced in this exothermic reaction caused the burning wire to remain incandescent at a steady state temperature that was estimated visually to be in the neighborhood of 1000°. The burning platinum filament viewed through the dark red vapors of PtF$_6$ was a strikingly awesome sight. Ultimately the outer wall of the Pyrex

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) The final draft of the paper was written at the Scientific Laboratory of the Ford Motor Company.

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