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# Mixed-Ligand Complexes of Palladium(II) with Chloride and Iodide[1]

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Received April 17, 1972

A spectrophotometric study of the mixed complexes of palladium(II) with chloride and iodide has been carried out. Studies of the replacement reactions between $PdCl_4{}^{2-}$ and $PdI_4{}^{2-}$, both of which are the limiting halide species of palladium under the condition of study, were performed using various spectral regions. The spectra of $PdCl_4{}^{2-}$ and $PdI_4{}^{2-}$ show peaks at 279 and 222 nm and at 268, 317, 407, and 487 nm, respectively. Formation constants (log $\dagger K$) have been determined for the various equilibria as follows: 3.95 ± 0.05 for $[PdCl_3I^{2-}][Cl^-]/[PdCl_4{}^{2-}][I^-]$, 4.1 ± 0.2 for $[PdCl_2I_2{}^{2-}][Cl^-]/[PdCl_3I^{2-}] \cdot [I^-]$, 2.8 ± 0.3 for $[PdClI_3{}^{2-}][Cl^-]/[PdCl_2I_2{}^{2-}][I^-]$, and 1.30 ± 0.05 for $[PdI_4{}^{2-}][Cl^-]/[PdClI_3{}^{2-}][I^-]$. The method of calculation was based on some previously derived functions, which allow the characterization of the whole system with a minimum manipulation of the data and a minimum use of the previously determined parameters. The individual spectra for the mixed species have been resolved using the calculated constants. This investigation represents the last in the series involving palladium with chloride, bromide, and iodide. Some interesting correlations are presented.

Introduction

The treatment of spectrophotometric data in a system of mixed-ligand complexes involving replacement reactions (eq 1) was discussed in earlier publications.[2]

$$MX_N + nY = MX_{N-n}Y_n + nX \qquad (1)$$
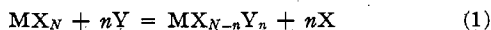
(N is the maximum coordination number of the metal ion; $n = 1, 2, \ldots, N$; X and Y are the two ligands.) Functions were derived which enable the calculation of the stepwise equilibrium constants in such systems using the original data in a simple way. Studies on the palladium–chloride–bromide system and the palladium–bromide–iodide system have been presented in previous publications.[2] This paper describes similar studies on a series of consecutive mixed-ligand complexes of palladium(II) with chloride and iodide.

Experimental Section

Apparatus.—A Cary Model 14 recording spectrophotometer was used for obtaining the absorption spectra of various solutions. Special cell assemblies as described previously[2] were employed, when necessary, to avoid problems due to the air oxidation of iodide in acidic media. Different cell path lengths were used to get optimum absorbances in different experiments.

Materials.—Engelhard Industries, Inc., palladium chloride was used to prepare a standard stock solution of palladium as described earlier.[2a] The following other reagents were used to make appropriate stock solutions: perchloric acid (Baker analyzed reagent), reagent grade anhydrous lithium chloride (Baker and Adamson), anhydrous lithium perchlorate (G. Frederick Smith), and lithium iodide (Mallinckrodt Chemical Works). Air-free solutions of lithium iodide were prepared and stored under a N_2 atmosphere as described.[2b]
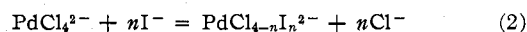
Absorbance Curves.—It was found through earlier experiments that solutions containing 5×10^{-5} M palladium at an ionic

(1) This work was performed under the auspices of the United States Atomic Energy Commission.

(2) (a) S. C. Srivastava and L. Newman, Inorg. Chem., 5, 1506 (1966); (b) S. C. Srivastava and L. Newman, ibid., 6, 762 (1967).

strength of 4.5 showed no further change in absorbance with a concentration higher than 1.0 M chloride or 1.0 M iodide. The limiting halide species of palladium, $PdCl_4{}^{2-}$ and $PdI_4{}^{2-}$, show absorption maxima at 222 and 279 nm and at 268, 317, 407, and 487 nm, respectively. The absorbance curves of $PdI_4{}^{2-}$ and $PdCl_4{}^{2-}$ are shown in Figure 1. As in the case of the palladium–bromide–iodide system, different regions of the spectral curves also had to be used in this system for evaluating the different equilibrium constants. There are no two corresponding peaks that could be used unequivocally to study all the constants. Furthermore, the problems due to the low solubility of PdI_2 also had to be minimized. This necessitated the use of very low concentrations of the metal ion so that the amount of PdI_2 formed was very small so as not to exceed the solubility limit. As a consequence, in many experiments with low metal ion concentration, 100-mm cells were used to obtain sufficient absorbance. The spectral regions chosen for study were ones with high relative intensities of the peaks.

A series of spectra were run using different concentrations of palladium each with varying ratios of halides. The solutions had the following composition: palladium (concentrations between 2×10^{-6} and 4×10^{-4} M in different experiments), 0.1 M H⁺ (HClO₄), 2.4 M LiClO₄, and varying ratios of iodide to chloride. The total halide was kept constant at 2.0 M and, thus, the ionic strength was maintained at 4.5. Suitable blanks with the same composition, except that the metal ion was absent, were used.

Results and Discussion

According to reaction 1, the equilibria existing in the palladium–chloride–iodide system may be represented by the equation

$$PdCl_4{}^{2-} + nI^- = PdCl_{4-n}I_n{}^{2-} + nCl^- \qquad (2)$$

with the overall constants defined as

$$\dagger\beta_n = \frac{[PdCl_{4-n}I_n{}^{2-}][Cl^-]^n}{[PdCl_4{}^{2-}][I^-]^n} \qquad (3)$$

The stepwise equilibria can be written as

$$PdCl_{5-n}I_{n-1}{}^{2-} + I^- = PdCl_{4-n}I_n{}^{2-} + Cl^- \qquad (4)$$

$$\dagger K_n = \frac{[PdCl_{4-n}I_n{}^{2-}][Cl^-]}{[PdCl_{5-n}I_{n-1}{}^{2-}][I^-]} \qquad (5)$$

A detailed description of all terms utilized in this paper has been published.[3]

It is obvious that starting with both $PdCl_4{}^{2-}$ and then with $PdI_4{}^{2-}$, only two step replacement reactions need be studied to characterize the system completely.

Evaluation of the First Step Constant.—The method for the determination of the step formation constant for the first replacement reaction was the same as described previously.[2a] The data were plotted as A vs. $\log R$ (A, the measured absorbance of a mixture; R, the ratio $Y/X = [I^-]/[Cl^-]$ when starting from the chloride side and equal to $[Cl^-]/[I^-]$ when starting with $PdI_4{}^{2-}$). These plots were compared with a family of normalized curves and fitted on the appropriate curves. The translation in the abscissa gave the value of $\dagger\beta_1$ and the translation in the ordinate gave A_1 (the absorbance, if all the palladium were as PdX_3Y^{2-}). Different wavelengths were used for these calculations. Data as shown in Figure 2 were used for the calculation of the formation constant of $PdCl_3I^{2-}$ starting from $PdCl_4{}^{2-}$. The air oxidation of iodide did not present any problems due to the extremely low concentration of iodide used in this experiment. By using 100-mm cells, a concentration of palladium as low as 1.5×10^{-5}
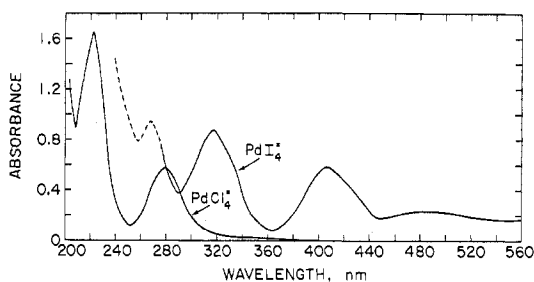

Figure 1.—Absorbance curves of $PdI_4{}^{2-}$ and $PdCl_4{}^{2-}$. $[Pd^{2+}] = 5.0 \times 10^{-5}$ M, path length 10 mm, total halide 1.0 M (Cl^-), 1.6 M (I^-), and ionic strength 4.0.

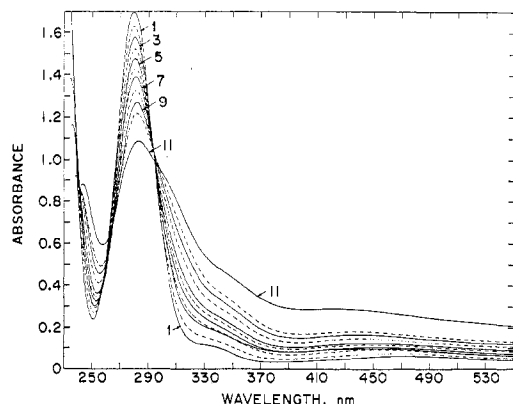

Figure 2.—Absorption spectra of 1.5×10^{-5} M palladium (100-mm cells) at ionic strength 4.5. Composition of the solutions: 0.1 M $HClO_4$, 2.4 M $LiClO_4$, and 2.0 M ($LiI + LiCl$). Log R ($R = [I^-]/[Cl^-]$) in various curves is given below.

Curve	Log R	Curve	Log R	Curve	Log R	Curve	Log R
1	No iodide	4	−4.673	7	−4.375	10	−4.082
2	−5.147	5	−4.549	8	−4.253	11	−3.961
3	−4.847	6	−4.453	9	−4.158		

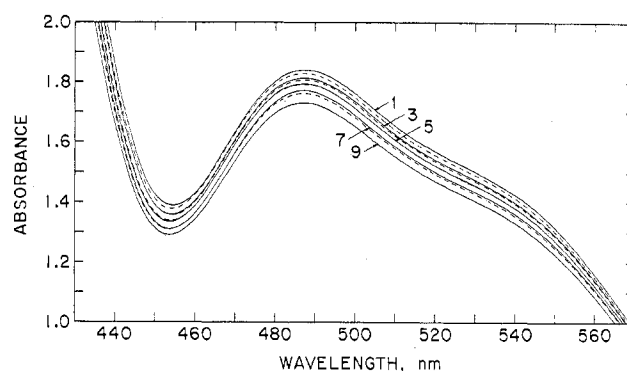(3) T. W. Gilbert and L. Newman, *Inorg. Chem.*, **9**, 1705 (1970).

Figure 3.—Absorption spectra of 4.0×10^{-4} M palladium (10-mm cells) at ionic strength 4.5. Composition of the solutions: 0.1 M $HClO_4$, 2.4 M $LiClO_4$, and 2.0 M ($LiI + LiCl$). Log R ($R = [Cl^-]/[I^-]$) in various curves is given below.

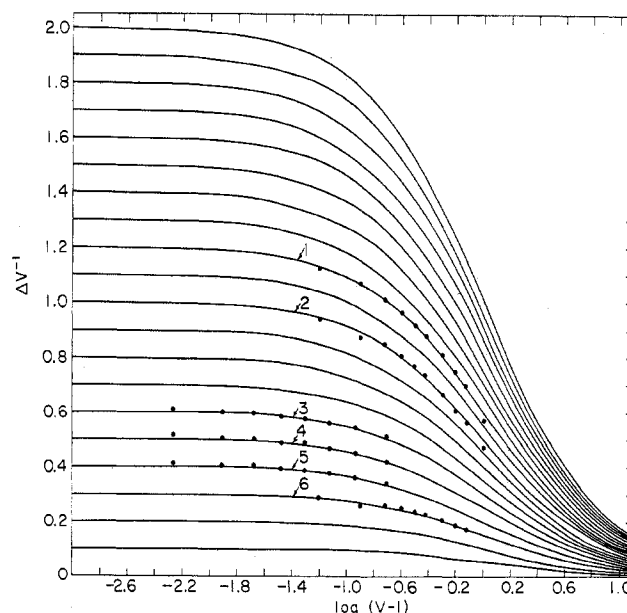| Curve	Log R	Curve	Log R	Curve	Log R	Curve	Log R
1	No chloride	4	−0.3680	6	0.000	9	0.6021
2	−0.9547	5	−0.1760	7	0.1760		
3	−0.6021			8	0.3680		

Figure 4.—The family of normalized curves: $\Delta V^{-1} = A - A_1$; $\log (V - 1) = \log R + \log \beta_1$. Some typical plots of A vs. $\log R$ at various wavelengths shown fitted onto appropriate curves.

(i) Formation of $PdCl_3I^{2-}$ from $PdCl_4{}^{2-}$

Curve	Wavelength, nm	Curve	Wavelength, nm
1	280	6	440
2	320		

(ii) Formation of PdI_3Cl^{2-} from $PdI_4{}^{2-}$

Curve	Wavelength, nm	Curve	Wavelength, nm
3	485	5	550
4	495		

M could be used to obtain sufficient absorbance. A titration type procedure was employed, the chloride was kept constant at 2.0 M, and the iodide was added in extremely small increasing amounts. Curves 1–9 and a number of wavelengths in the regions 250–290 and 310–410 nm were used for the calculations.

The curves shown in Figure 3 were employed for the calculation of the formation constant for PdI_3Cl^{2-} starting from the iodide side. A special cell assembly

Figure 5.—Absorption spectra of 2.0×10^{-6} M palladium (100-mm cells) at ionic strength 4.5. Composition of the solutions: 0.1 M HClO$_4$, 2.4 M LiClO$_4$, and 2.0 M (LiI + LiCl). Log R ($R = [I^-]/[Cl^-]$) in various curves is given below.

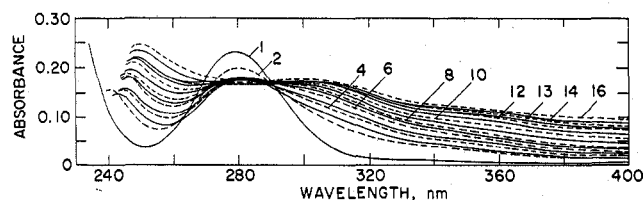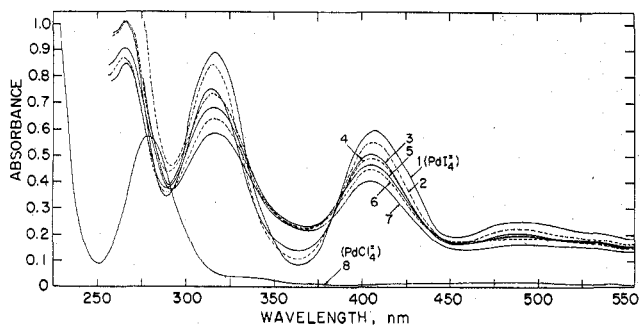| Curve	Log R	Curve	Log R	Curve	Log R	Curve	Log R
1	No iodide	5	-3.9547	9	-3.7404	13	-3.5740
2	-4.2899	6	-3.8938	10	-3.6917	14	-3.5316
3	-4.1355	7	-3.8450	11	-3.6536	15	-3.5006
4	-4.0315	8	-3.8044	12	-3.6220	16	-3.4585

Figure 6.—Absorption spectra of 5.0×10^{-6} M palladium (100-mm cells) at ionic strength 4.5. Composition of the solutions: 0.1 M HClO$_4$, 2.4 M LiClO$_4$, and 2.0 M (LiI + LiCl). Log R ($R = [Cl^-]/[I^-]$) in various curves is given below.

Curve	Log R	Curve	Log R	Curve	Log R	Curve	Log R
1	No chloride	3	1.8384	5	2.1427	7	2.2430
2	1.4316	4	2.0386	6	2.2017	8	No iodide

as described earlier[2b] was employed to minimize chances of the air oxidation of iodide. The whole experimentation was carried out under an atmosphere of nitrogen. A palladium concentration of 4.0×10^{-4} M, cells with 10-mm path length, and the PdI$_4{}^{2-}$ peak at 487 nm provided the best data for the calculation of this constant. Curves 1–9 were used. The change in absorbance of solutions of PdI$_4{}^{2-}$ with successive additions of PdCl$_4{}^{2-}$ was very small and a very large ratio [Cl$^-$]/[Br$^-$] was required before the formation of PdI$_3$Cl^{2-} was appreciable. The absorbance at other regions of the PdI$_4{}^{2-}$ spectrum did not change significantly. The absorbance due to PdCl$_4{}^{2-}$ itself being almost zero in this wavelength region, data around the 487-nm peak were found to be best suited for the calculation of $\dagger\beta_1$ for PdI$_3$Cl^{2-}.

The values of $\dagger K_1$ ($\dagger\beta_1$ for PdCl$_3$I^{2-}) and $\dagger K_4$ ($1/\dagger\beta_1$ for PdI$_3$Cl^{2-}) thus measured were self-consistent in that no variation with wavelength was observed. The average values of these constants were used to determine A_1 (the absorbance of PdI$_3$Cl^{2-} or PdCl$_3$I^{2-}) by translation in the ordinate using normalized curves. A few typical plots of A vs. log R at various wavelengths are shown fitted onto the appropriate normalized curves in Figure 4.

Evaluation of the Second Step Constant.—The data for the calculation of the formation constant for PdCl$_2$I$_2{}^{2-}$ starting with either PdCl$_4{}^{2-}$ or PdI$_4{}^{2-}$ was very difficult to obtain due to the very low solubility of PdI$_2$. In the experiments utilized for the determina-
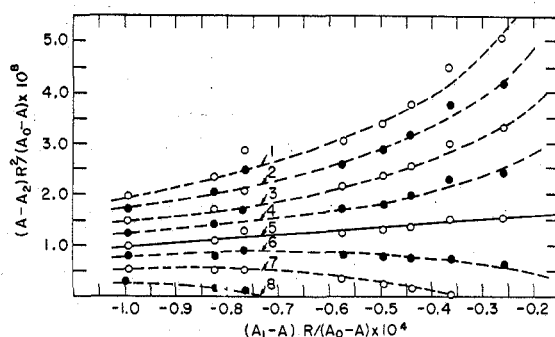

Figure 7.—A typical plot for the determination of the constant for the reaction PdX$_4{}^{2-}$ + 2Y$^-$ $\rightleftarrows$ PdX$_2$Y$_2{}^{2-}$ + 2X$^-$. Determination of the formation constant for PdCl$_4{}^{2-}$ + 2I$^-$ $\rightleftarrows$ PdCl$_2$I$_2{}^{2-}$ + 2Cl$^-$; 320 nm. Various assumed values of A_2 are given below.

Curve	A_2	Curve	A_2	Curve	A_2	Curve	A_2
1	0.275	3	0.225	5	0.175	7	0.125
2	0.250	4	0.200	6	0.150	8	0.100

tion of the constants for PdX$_3$Y^{2-}, it was observed that whenever the concentration of iodide was increased so as to allow the formation of PdI$_2$Cl$_2{}^{2-}$ in significant amounts, a precipitate of PdI$_2$ appeared. Although hardly visible to the naked eye, the solutions became colloidal enough to cause rapid and irregular variations in absorbance. The situation was most troublesome when starting from the chloride side.

Data could be obtained starting with PdI$_4{}^{2-}$ when the concentration of Pd is in the range of $(3-8) \times 10^{-6}$ M. Under these conditions, incremental additions of PdCl$_4{}^{2-}$ permitted significant formation of PdI$_2$Cl$_2{}^{2-}$ before PdI$_2$ began to precipitate. Thus, by using very low concentrations of the metal ion and by employing 100-mm cells, it became possible to obtain data for measuring the constants for PdX$_2$Y$_2{}^{2-}$. A large number of experiments with varying techniques were performed before the optimum conditions could be found.

As described earlier,[2a] a minimum use of the previously determined parameters was attempted for the calculation of the constant for PdX$_2$Y$_2{}^{2-}$. The following derivation was used for obtaining suitable plots for the calculations

$$\frac{(A - A_2)R^2}{(A_0 - A)} = \dagger\beta_2{}^{-1} + \frac{R(A_1 - A)}{(A_0 - A)}\dagger\beta_1\dagger\beta_2{}^{-1} \quad (6)$$

The terms have the meaning already described.[2a] A number of assumed values of A_2 were substituted in this equation (A, A_0, R are directly measurable quantities) and the left term was plotted against $R(A_1 - A)/(A_0 - A)$ (the previously derived value of A_1 was used). A straight line was obtained only when using the correct value of A_2. The slope of this line gave the value of $\dagger K_2{}^{-1}$ and the intercept provided the value for $\dagger\beta_2{}^{-1}$. Values of $\dagger\beta_1$ could also be calculated from these plots ($\dagger\beta_2/\dagger K_2$) and these checked with the previously determined values using the normalized curves.

Figure 5 shows the spectral curves obtained with 2.0×10^{-6} M Pd using 100-mm cells and employing the titration technique. Curves 3–14 in this figure were used to calculate $\dagger K_2$ for PdCl$_2$I$_2{}^{2-}$ from the chloride side. Various wavelengths were used in the wavelength regions 245–260 and 310–380 nm. An attempt was made to use higher palladium concentrations in this experiment so as to be able to obtain higher absor-

bances, but a turbidity always appeared in the solutions due to the formation of PdI_2, when a concentration of Pd $> 2 \times 10^{-6}$ M was employed. The formation constant for $PdI_2Cl_2{}^{2-}$ starting from the iodide side was calculated using the data shown in Figure 6. Due to the same reasons as described above, a concentration 5×10^{-6} M of palladium was used and 100-mm cells were employed so as to obtain sufficient absorbance. Due to the presence of large amounts of iodide to start with, a titration experiment was not feasible and the special cell assembly[2b] was used to prevent the air oxidation of iodide. Individual mixtures had to be prepared and their spectra recorded. The value of the constant for $PdI_2Cl_2{}^{2-}$ obtained using these data had a larger uncertainty (~ 0.3 log unit) as compared to the other constants; this was due to the inherent experimental errors while trying to obtain these data.

Figure 7 shows a typical plot for the calculation of the second step constant. A number of such plots were made from both the chloride and the iodide sides.

The last four values given in Table I are averages of the values obtained for the formation constants.

Figure 8.—Resolved spectra of palladium–chloride–iodide mixed complexes. $[Pd^{2+}] = 1.5 \times 10^{-4}$ M; ionic strength 4.5. The absorption maxima (and the associated molar absorptivities $\times 10^{3}$) are the following: $PdCl_4{}^{2-}$ 222 $\pm$ 1 (33.1 $\pm$ 0.1), 279 $\pm$ 1 (11.2 $\pm$ 0.05); $PdCl_3I^{2-}$ 310 $\pm$ 5 (8.65 $\pm$ 0.15), 430 $\pm$ 5 (2.20 $\pm$ 0.10); $PdCl_2I_2{}^{2-}$ 345 $\pm$ 5, 435 $\pm$ 3; $PdClI_3{}^{2-}$ 315 $\pm$ 5 (16.3 $\pm$ 0.2), 407 $\pm$ 3 (10.3 $\pm$ 0.2), 490 $\pm$ 5 (4.00 $\pm$ 0.1); $PdI_4{}^{2-}$ 487 $\pm$ 1 (4.68 $\pm$ 0.05), 407 $\pm$ 1 (11.9 $\pm$ 0.1), 317 $\pm$ 1 (17.6 $\pm$ 0.05), 268 $\pm$ 2 (22.4 $\pm$ 0.2).

TABLE I
COMPILATION OF THE FORMATION CONSTANTS

Reaction	Log $\dagger\beta_n$	Symbol
$PdCl_4{}^{2-} + Br^- = PdCl_3Br^{2-} + Cl^-$	1.55 ± 0.05	L – X
$PdCl_4{}^{2-} + 2Br^- = PdCl_2Br_2{}^{2-} + 2Cl^-$	2.64 ± 0.10	X
$PdCl_4{}^{2-} + 3Br^- = PdClBr_3{}^{2-} + 3Cl^-$	3.59 ± 0.10	S
$PdCl_4{}^{2-} + 4Br^- = PdBr_4{}^{2-} + 4Cl^-$	4.14 ± 0.10	L
$PdBr_4{}^{2-} + I^- = PdBr_3I^{2-} + Br^-$	2.75 ± 0.05	2L – Y
$PdBr_4{}^{2-} + 2I^- = PdBr_2I_2{}^{2-} + 2Br^-$	5.75 ± 0.15	Y
$PdBr_4{}^{2-} + 3I^- = PdBrI_3{}^{2-} + 3Br^-$	7.45 ± 0.20	T
$PdBr_4{}^{2-} + 4I^- = PdI_4{}^{2-} + 4Br^-$	8.25 ± 0.20	2L
$PdCl_4{}^{2-} + I^- = PdCl_3I^{2-} + Cl^-$	3.95 ± 0.05	3L – (X + Y)
$PdCl_4{}^{2-} + 2I^- = PdCl_2I_2{}^{2-} + 2Cl^-$	8.05 ± 0.20	X + Y
$PdCl_4{}^{2-} + 3I^- = PdClI_3{}^{2-} + 3Cl^-$	10.85 ± 0.35	S + T
$PdCl_4{}^{2-} + 4I^- = PdI_4{}^{2-} + 4Cl$	12.15 ± 0.35	3L

Conclusions

The individual spectra of various mixed species were calculated using the constants thus obtained. Unlike the chloride–bromide system[2a] and the bromide–iodide system[2b] the calculation of the spectrum for the middle species ($PdI_2Cl_2{}^{2-}$ in this system) was not possible due to the large limit of error on the value of $\dagger K_3$. Absorbance values of this middle species (A_2) at various wavelengths had different values depending on whether calculations were made starting from the chloride side or the iodide side. However, the wavelengths of maximum absorption occupied the same position when calculated from either side. A correct assignment of the spectrum for $PdCl_2I_2{}^{2-}$ thus was not possible.

The final spectra are shown in Figure 8. The absorption maxima and the molar absorptivities of the various species are given in the figure legend.
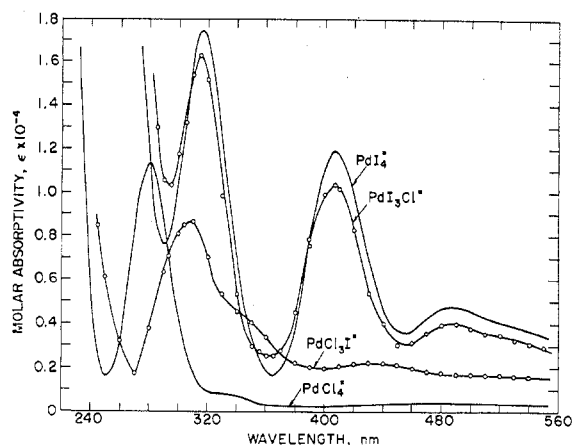
Table II shows the formation constants of the three
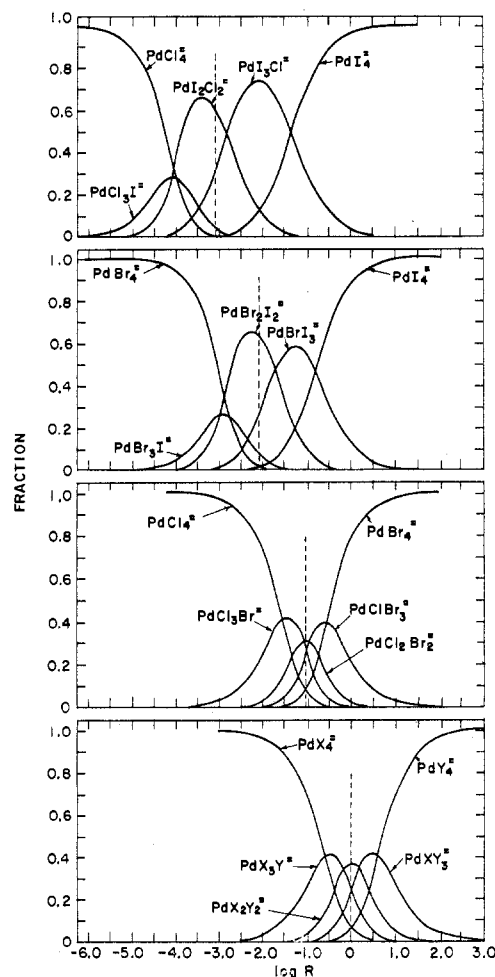

Figure 9.—The relative distribution of various mixed palladium–halide species as a function of log R: top figure, chloride–iodide mixed complexes; second from top, bromide–iodide mixed complexes; second from bottom, chloride–bromide mixed complexes; and bottom figure, assuming statistical random distribution.

TABLE II
STATISTICAL AND THE OBSERVED VALUES OF THE FORMATION CONSTANTS

		Log (equilibrium constant)		
Reaction	Statistical	X = Cl⁻ Y = Br⁻	X = Br⁻ Y = I⁻	X = Cl⁻ Y = I⁻
$^3/_4\text{PdX}_4{}^{2-} + ^1/_4\text{PdY}_4{}^{2-} = \text{PdX}_3\text{Y}^{2-}$	0.60	0.52 ± 0.05	0.69 ± 0.07	0.91 ± 0.10
$^1/_2\text{PdX}_4{}^{2-} + ^1/_2\text{PdY}_4{}^{2-} = \text{PdX}_2\text{Y}_2{}^{2-}$	0.78	0.57 ± 0.06	1.62 ± 0.11	1.98 ± 0.18
$^1/_4\text{PdX}_4{}^{2-} + ^3/_4\text{PdY}_4{}^{2-} = \text{PdXY}_3{}^{2-}$	0.60	0.49 ± 0.05	1.26 ± 0.07	1.74 ± 0.10

mixed species starting from the parent reactants for the Cl/I system along with the Br/Cl and I/Br systems and including the statistically predicted values. It should be pointed out that the statistical values assume that isomers for square $\text{PdX}_2\text{Y}_2{}^{2-}$ are present in the statistically expected relative amounts (that is equivalent to assuming a tetrahedral configuration and, therefore, no isomers).

As may be seen, there is an enhancement in the values of the constants in this system over the statistically predicted values. It is interesting to note that in the chloride–bromide system, the measured values were fairly close to the statistical values. In the bromide–iodide system, the measured constants were slightly higher than the statistical constants, but the enhancement was not as much as in the present chloride–iodide system.

The relative distributions of the various species in each of the three systems that have been studied are shown as a function of log R in Figure 9. The curves in the bottom plot show the statistical distribution and the position on the abscissa is determined by assuming $\beta_{4(Y)} = \beta_{4(X)}$. The observed differences can be normalized by shifting these curves such that there is a superimposition of the dashed lines.

A compilation of the formation constants for the three systems is given in Table I. First it should be recognized that

$$\dagger\beta_4 = \frac{\beta_{4(Y)}'}{\beta_{4(X)}}$$

where

$$\beta_{4(Y)} = \frac{[\text{PdY}_4{}^{2-}]}{[\text{Pd}^{2+}][\text{Y}^-]^4}$$

and $\beta_{4(X)}$ has the corresponding meaning. The mixed-ligand complexity constants yield a value for the ratio of the β_4's of the simple complexes based on the measurement of only four constants, as opposed to the

necessity of measuring eight constants if the ratio were to be calculated from the measurement of the simple β_4's. Consequently a more reliable measure of the relative stability of the halide complexes is obtained by studying mixed-ligand systems. Furthermore, the values or $\dagger\beta_4$ obtained from any two systems allows a prediction of the value for the third. As an example, the predicted value of log $\dagger\beta_4$ of 12.39 for the I⁻/Cl⁻ system is in excellent agreement with the measured value of 12.15. This is a clear and critical demonstration of the internal consistency of our measurements. Since the order of the constants is I⁻ > Br⁻ > Cl⁻, palladium is an element which falls into class b or which is a soft acceptor with respect to the halides as donors.

Some interesting correlations between these constants have already been noted[4] but they are worth repeating here. The correlations are summarized by the symbols shown for the log of the constants in Table I. As an example of how to treat these symbols: log $\dagger\beta_{1(I,Cl)} = 3.95 \approx 12.15 - 8.05$, or $\approx 3(4.14) - 2.64 - 5.75$, etc. One consequence of these correlations is that

$$[\text{PdBr}_4{}^{2-}] \approx \frac{[\text{PdCl}_3\text{Br}^{2-}][\text{PdBr}_3\text{I}^{2-}]}{[\text{PdCl}_3\text{I}^{2-}]} \approx$$

$$\frac{[\text{PdClBr}_3{}^{2-}][\text{PdBrI}_3{}^{2-}]}{[\text{PdClI}_3{}^{2-}]} \approx \frac{[\text{PdCl}_2\text{Br}_2{}^{2-}][\text{PdBr}_2\text{I}_2{}^{2-}]}{[\text{PdCl}_2\text{I}_2{}^{2-}]}$$

These correlations might simply arise from the coincidental fact that $2 \log \dagger\beta_{4(Br,Cl)} = 8.28 \approx \log \dagger\beta_{4(I,Br)} = 8.25$, but just why the rest should follow is not apparent. Since this is the only system of its type where such complete data are available, we are not able to ascertain whether these correlations have any general significance. As data for other systems become available, it will be most interesting to examine them with these concepts in mind.

(4) L. Newman and S. C. Srivastava, *Proc. Symp. Coord. Chem., 3rd, 1970,* **1,** 171 (1970).