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Kinetics, Mechanism, and Equilibrium for Formation/Cleavage of a Dinuclear Iodide-Bridged Complex of Palladium(II)

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Received January 13, 1977 AIC700244

The kinetics and equilibrium for eq 1 with the equilibrium constant $K_{26} = k_f[I^-]^2/k_d$ have been studied at 25.0 °C in 1.00 M sodium perchlorate medium. Measurements of the solubility of $PdI_2(s)$ in iodide solutions with $0.02 \leq [I^-] \leq 0.100$ M indicated PdI_4^{2-} and $Pd_2I_6^{2-}$ as the predominant complexes in this concentration range. Spectrophotometric equilibrium measurements, evaluated by a least-squares minimizing program, gave $K_{26} = 21 \pm 1$ M and the stepwise stability constant for PdI_4^{2-}, i.e., $K_4 = [PdI_4^{2-}]/[PdI_3H_2O^-][I^-] = 360 \pm 60\ M^{-1}$. The experiments gave no evidence for complexes with a mean ligand number greater than four. Stopped-flow experiments indicated a rate law for the equilibration between Pd(II) iodo complexes and $Pd_2I_6^{2-}$ of the form $d[Pd_2I_6^{2-}]/dt = k_f[PdI_4^{2-}]^2 - k_d[Pd_2I_6^{2-}]$, where $k_f = K_{26}c + K_{26}b/[I^-] + K_{26}a/[I^-]^2$, and $k_d = a + b[I^-] + c[I^-]^2$. The parameters are $a = 0.24 \pm 0.07\ s^{-1}$, $b = 4.3 \pm 0.6\ s^{-1}\ M^{-1}$, and $c = 15.5 \pm 0.9\ s^{-1}\ M^{-2}$. The mechanism for the formation of $Pd_2I_6^{2-}$ involves dimeric transition states, probably with double iodide bridges. The three terms in the rate expression indicate three parallel reaction paths for the formation of $Pd_2I_6^{2-}$ from PdI_4^{2-} and $PdI_3H_2O^-$.

Introduction

We have previously described kinetics and equilibria for the stepwise formation and dissociation of square-planar palladium(II)–chloro and –bromo complexes.[1] Equilibrium studies on the palladium(II) iodide system are complicated by low solubility of PdI_2, redox processes, especially in acidic solutions, formation of dinuclear species, and high stabilities. Except for early studies by Tananaev,[2] Schukarev,[3] and Grinberg[4,5] and co-workers, which are incomplete and partly discordant, equilibrium data seem to be lacking. No quantitative kinetic studies on palladium(II)–iodo complexes have appeared in the relevant literature.

The present paper describes the kinetics and mechanism for the formation and dissociation of the dinuclear complex $Pd_2I_6^{2-}$ according to

$$2PdI_4^{2-} \underset{k_d}{\overset{k_f}{\rightleftarrows}} Pd_2I_6^{2-} + 2I^- \qquad (1)$$

Preparation, structure, and spectra of dinuclear complexes of this type, $Pd_2X_6^{2-}$ (X = Cl, Br, I), have been described previously.[6-9]

In this context, we will also report spectrophotometric equilibrium measurements and measurements of the solubility of $PdI_2(s)$ in iodide solutions, which together give the equilibrium constants for reactions 1 and 2

$$PdI_3H_2O^- + I^- \rightleftarrows PdI_4^{2-} + H_2O \qquad (2)$$

i.e.

$$K_{26} = [Pd_2I_6^{2-}][I^-]^2/[PdI_4^{2-}]^2 = k_f[I^-]^2/k_d \qquad (3)$$

and

$$K_4 = [PdI_4^{2-}]/([PdI_3H_2O^-][I^-]) \qquad (4)$$

Experimental Section

Chemicals and Solutions. Palladium(II) perchlorate solutions in 1.00 M perchloric acid were prepared from palladium sponge (Johnson and Matthey, Spec. pure) according to ref 1a. Solid palladium iodide was precipitated by mixing a 25–50 mM palladium perchlorate solution in 1.00 M perchloric acid with an equal volume of an aqueous solution containing a stoichiometric amount of sodium iodide (Merck p.a.). The precipitate was filtered off, washed with ethanol and ether, and dried for 15 h at 90 °C. Gravimetric analysis indicated a quantitative precipitation of palladium as $PdI_2(s)$. The precipitate was very fine crystalline. Before use in the solubility measurements, it was refluxed at room temperature for 2–3 days with a 0.1 M sodium iodide solution. X-Ray powder photographs indicated a reproducible crystalline structure of the obtained palladium iodide (cf. ref 10 and 11).

A stock solution of palladium iodide complexes with $C_{Pd} = 1.66 \times 10^{-3}$ M and $C_I = 1.016$ M was prepared by addition of a weighed amount (about 300 mg) of $PdI_2(s)$ to a 500-mL volumetric flask, wrapped in aluminum foil to exclude light and containing 50 g of sodium iodide (Merck Suprapur) dissolved in 50 mL of boiled, doubly distilled water, flushed with nitrogen to remove dissolved oxygen. The palladium iodide dissolved quantitatively within 15 min; 25 g of sodium iodide (Suprapur) dissolved in 100 mL of water was added and the volume finally adjusted with nitrogen-flushed water to 500 mL. The solution was kept in the dark under nitrogen at about 4 °C in a refrigerator to avoid oxidation of iodide (cf. ref 12). Its absorption spectrum was constant and no precipitation was observed even after several months. The solution was analyzed for Pd by atomic absorption, which indicated a quantitative dissolution of the palladium iodide, and for iodide by titration with silver.

Iodide stock solutions were prepared immediately before use from sodium iodide (Merck Suprapur) and nitrogen-flushed water and were protected from illumination. All solutions had the ionic strength 1.00 M with sodium perchlorate (Baker's *p.a.* recrystallized once) as supporting electrolyte. The sodium perchlorate solutions had a pH of $3.8 < pH < 4.3$, so there was no risk of formation of periodate from the iodide.

The water was doubly distilled from quartz vessels. All solutions were flushed with nitrogen to prevent oxidation of iodide. All glassware was rinsed with aqua regia to prevent precipitation of $PdI_2(s)$ in supersaturated solutions.

Apparatus. Spectra were recorded using Cary 15 and Cary 118 instruments. The Cary 118 was used for the palladium analyses in the solubility study and for the spectrophotometric equilibrium measurements.

The stopped-flow instrument used for the kinetics was built at our institute. The principal parts were a modified Durrum-Gibson flow system with a pneumatic syringe drive and an accurately water-thermostated flow system (±0.1 °C), combined with a spectrophotometer unit from Messanlagen, Göttingen, having a Bausch and Lomb 27000 grating monochromator, catalog no. 33-86-01. The display unit was a Tektronix single beam storage oscilloscope D 15 with a 5A20N differential amplifier and a 5B10N time base amplifier and a Polaroid camera. The dead-time of the instrument was 2–3 ms.

Solubility Measurements. The solubility of $PdI_2(s)$ at 25.0 °C was measured in the interval $20 \leq [I^-] \leq 100$ mM using a thermostated solubility column with an inner diameter of 8 mm, filled with a ca. 10-mm thick layer of PdI_2 precipitate, which was supported by a G4 glass filter disk. The apparatus and procedure have been described by Johansson.[13] After equilibration, the iodide concentration of the solutions was adjusted to 100 or 30 mM by addition of 0.5 M sodium iodide. The absorbance spectrum was recorded in the interval 450–290 nm where PdI_4^{2-} has two absorption bands (cf. Figure 1c). The absorbance curve was numerically integrated and the palladium concentration calculated from the value of the integral by comparison

Table I. Spectrophotometric Equilibrium Measurements

Series	C_I/mM	$10^5 C_{Pd}$/M	e/cm^{-1} ^{a} 340 nm	335 nm	330 nm
a	26.9	4.40	0.577	0.676	0.732
a	30.8	4.40	0.548	0.650	0.714
a	34.7	4.40	0.519	0.624	0.692
a	42.5	4.40	0.465	0.572	0.650
a	54.2	4.40	0.411	0.520	0.616
a	81.4	4.40	0.333	0.442	0.555
b	50.8	8.32	0.94	1.13	1.26
b	50.8	6.65	0.716	0.87	0.98
b	50.8	4.99	0.485	0.600	0.699
b	50.8	3.33	0.295	0.374	0.447
b	50.8	1.660	0.121	0.160	0.203
b	50.8	0.832	0.049	0.069	0.092
b	50.8	0.249	0.012	0.018	0.026
c	101.6	16.60	1.57	1.98	2.31
c	101.6	13.30	1.19	1.52	1.80
c	101.6	9.98	0.83	1.08	1.31
c	101.6	8.32	0.656	0.86	1.06
c	101.6	6.65	0.500	0.666	0.84
c	101.6	4.99	0.349	0.474	0.607
c	101.6	2.990	0.185	0.253	0.346
c	101.6	2.000	0.115	0.164	0.224
c	101.6	0.998	0.051	0.074	0.106
c	101.6	0.832	0.042	0.064	0.090
c	101.6	0.499	...	0.035	0.051

[a] e denotes the absorptivity corrected for the I_3^- absorbance at the three wavelengths used for the least-squares calculation.

with separately performed calibration experiments with known concentrations of palladium. Palladium concentrations as low as 10^{-6} M could be analyzed with an accuracy of about ±2%. The following values for the solubility were obtained ($10^3 C_I$/M, $10^6 C_{Pd}$/M): 20.00, 0.52; 30.0, 1.20; 30.0, 1.20; 50.0, 3.25; 50.0, 3.32; 70.0, 6.4; 100.0, 12.9.

Spectrophotometric Equilibrium Measurements. The spectra of the solutions listed in Table I were recorded at 25.0 °C in the region 280–450 nm using 0.200–10.00-cm cells. The reference cell contained water. To avoid precipitation of $PdI_2(s)$ in supersaturated solutions, they were mixed in the following way. For series a, 1.36 mL of the palladium stock solution with $C_{Pd} = 1.66$ mM and $C_I = 1.016$ M was quickly transferred to 50-mL sodium iodide–sodium perchlorate solutions which had the concentrations of free iodide 0.00, 5.00, 10.00, 28.00, and 56.0 mM and which were prepared by dilution of a 200.0 mM sodium iodide stock solution.

The first solutions in series b and c were obtained by dilution of the 1.66 mM palladium stock solution 20 or 10 times with 1.00 M sodium perchlorate. The other solutions in these series were prepared by mixing the preceding solution with sodium iodide–sodium perchlorate stock solutions with $C_{NaI} = 50.8$ mM and $C_{NaClO_4} = 0.95$ M for series b and $C_{NaI} = 101.6$ mM and $C_{NaClO_4} = 0.90$ M for series c.

Most solutions were stable for several hours, except those having the largest ratios C_{Pd}/C_I. Their absorbance decreased slowly because of precipitation. All spectra were therefore recorded immediately after mixing.

The concentration of I_3^- in the freshly prepared iodide stock solutions increased slowly with time. The absorbance of these solutions was recorded in the wavelength interval 450–290 nm before and after each experimental series. By use of the separately determined I_3^- spectrum included in Figure 1c their I_3^- concentrations were estimated to be less than about 5×10^{-7} M in all cases.

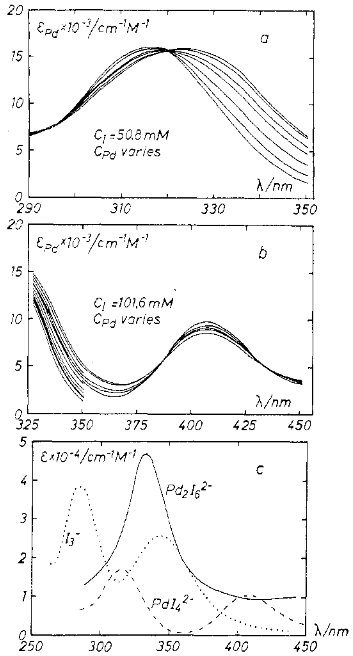

Figure 1. (a) Absorption spectra for the solutions in Table I, series b, corrected for the I_3^- absorbance. $\epsilon_{Pd} = e/C_{Pd}$. (b) The same for series c. (c) Spectra for $Pd_2I_6^{2-}$ (full-drawn) and PdI_4^{2-} (dashed) calculated from K_{26} and the spectra of the solutions in Table I using LETAGROP 4.[15] A separately recorded I_3^- spectrum is included (dotted).

Table II. Observed Rate Constants, k_{exptl}, for the Dissociation of $Pd_2I_6^{2-}$ and the Corresponding Values for k_d, Calculated from Eq 24

C_I/M	k_{exptl}/s^{-1}	k_d/s^{-1}
	$C_{Pd} = 1.55 \times 10^{-5}$ M	
0.0910	0.83, 0.85	0.72, 0.74
0.1576	1.35, 1.38	1.28, 1.31
0.224	2.16, 2.14	2.11, 2.09
0.291	2.67, 2.67	2.63, 2.63
0.357	3.49, 3.47	3.46, 3.44
0.612	8.84, 8.67	8.81, 8.64
0.808	14.4, 14.9	14.4, 14.9
1.004	17.2, 24.2	17.2, 24.2
	$C_{Pd} = 4.15 \times 10^{-5}$ M	
0.1254	1.28, 1.29	1.07, 1.07
0.225	2.05, 2.03	1.92, 1.90
0.325	3.49, 3.50	3.38, 3.39
0.425	4.99, 4.92	4.90, 4.83
0.525	6.82, 6.89	6.74, 6.81
0.607	9.59, 9.58	9.50, 9.49
0.800	13.3, 13.3	13.2, 13.2
0.995	18.7, 20.3	18.6, 20.2

Figures 1a and b show the spectra for the solutions in series b and c corrected for the I_3^- absorbance. It is obvious from the spectra that a suitable wavelength interval for calculation of the equilibrium constant K_{26} is 330–340 nm. Here, the difference in molar absorptivity between $Pd_2I_6^{2-}$ and PdI_4^{2-} is sufficiently large, and the molar absorptivity of I^- is negligible. The molar absorptivity of I_3^- is known, so a correction for the I_3^- absorbance can be applied. Table I gives the corrected absorptivities at the three wavelengths used for the calculations. The correction for the absorbance of I_3^- was of importance only for solutions measured in cells longer than 1 cm and was generally only a few percent of the observed absorbance, except in a few cases, where it amounted to 10 or 20%.

Kinetic Measurements. The stopped-flow experiments were performed under pseudo-first-order conditions at 340 nm, where $Pd_2I_6^{2-}$ has a molar absorptivity of 42 700 cm^{-1} M^{-1} and PdI_4^{2-} 4620 cm^{-1} M^{-1}; cf. Figure 1c. The first-order rate constants were calculated from the transmittance vs. time curves using a least-squares program.

The dissociation of $Pd_2I_6^{2-}$ described by k_d was followed by mixing one solution containing palladium (3.10×10^{-5} or 8.30×10^{-5} M), sodium iodide (48.7 or 50.8 mM), and sodium perchlorate (0.95 M) with another containing sodium iodide ($0.133 \le C_I \le 1.00$ M) and sodium perchlorate (1.00 M − C_I). The three experiments for the largest concentrations of iodide were performed by mixing one solution containing the same palladium and iodide concentrations as above but no sodium perchlorate with another solution containing sodium iodide ($C_I \approx 1.18$, 1.57, or 1.95 M) and sodium perchlorate (1.95 M − C_I). The heat of dilution in these three runs was negligible. In all these experiments, the concentration of iodide was sufficiently large to nearly suppress the reverse reaction, described by k_f. Table II summarizes the experiments.

Table III. Observed Rate Constants for the Relaxation Experiments

$10^5 C_{Pd}$/M	C_I/mM			$10^5 \times [PdI_4^{2-}]_{eq}$/M	k_{exptl}/s^{-1}
Soln I	Soln I	Soln II	Kinetics		(mean)
Concentration-Jump Experiments					
49.9	508	0	254	21.6	3.18
41.6	508	0	254	18.4	2.87
33.3	508	0	254	15.0	3.14
24.95	508	0	254	11.5	2.68
16.65	508	0	254	7.8	3.53
8.31	508	0	254	4.0	2.13
20.00	152.3	47.7	100	7.4	1.71
16.00	152.3	47.7	100	6.2	1.63
12.00	152.3	47.7	100	4.9	1.48
9.68	152.3	47.6[a]	100	4.0	1.34
7.74	152.3	47.6[a]	100	3.3	1.54
4.84	152.3	47.6[a]	100	2.16	1.15
13.26	101.6	30.0	65.8	4.5	1.31
9.98	101.6	30.0	65.8	3.6	1.20
8.32	101.6	30.0	65.8	3.1	1.17
6.65	101.6	30.0	65.8	2.57	1.17
4.99	101.6	30.0	65.8	2.02	1.12
3.33	101.6	30.0	65.8	1.41	1.03
10.50	84.0	15.60	49.8	3.3	1.24
9.00	84.0	15.60	49.8	2.9	1.70
7.50	84.0	15.60	49.8	2.52	1.24
6.00	84.0	15.60	49.8	2.12	1.00
4.50	84.0	15.60	49.8	1.68	0.98
3.00	84.0	15.60	49.8	1.19	0.81
7.50	65.0	10.00	37.5	2.17	1.24
6.00	65.1	10.00	37.5	1.84	1.09
4.50	65.1	10.00	37.5	1.48	1.00
3.00	65.1	10.00	37.5	1.07	0.80
1.500	65.1	10.00	37.5	0.60	0.76
8.32	50.8	10.00	30.4	2.05	1.06
6.65	50.8	10.00	30.4	1.75	1.12
4.99	50.8	10.00	30.4	1.43	0.90
4.16	50.8	10.00	30.4	1.25	1.00
3.33	50.8	10.00	30.4	1.06	0.70
2.50	50.8	10.00	30.4	0.85	0.63
Dilution Experiments					
16.6	101.6	0	50.8	4.6	1.38
11.6	101.6	0	50.8	3.5	1.25
10.0	101.6	0	50.8	3.2	1.25
5.00	101.6	0	50.8	1.84	0.86
4.00	101.6	0	50.8	1.53	0.98
3.00	101.6	0	50.8	1.20	0.92
2.00	101.6	0	50.8	0.84	0.87
16.6	101.6	0	50.8	4.6	1.69
10.00	101.0	0	50.5	3.2	0.96
6.64	100.6	0	50.3	2.3	1.28
4.98	100.5	0	50.3	1.83	0.82
3.32	100.3	0	50.2	1.30	0.83
1.66	100.2	0	50.1	0.71	0.79
4.50	40.0	0	20.0	1.02	0.97
3.60	40.0	0	20.0	0.87	1.17
3.00	40.0	0	20.0	0.77	1.24
2.40	40.0	0	20.0	0.66	0.83
1.80	40.0	0	20.0	0.53	0.70
1.20	40.0	0	20.0	0.39	0.66
0.60	40.0	0	20.0	0.22	0.50

[a] These solutions also contained palladium (1.45×10^{-6} M).

The formation of $Pd_2I_6^{2-}$ can be followed by decreasing the iodide concentration. Since the dimerization is second order with respect to PdI_4^{2-} (vide infra), the majority of the kinetic runs were designed as concentration-jump experiments in order to give simple first-order kinetics. Table III summarizes these experiments. The conversion of PdI_4^{2-} was ≤11%, which is small enough to fulfill the requirements for a first-order approximation.

Some kinetic runs were arranged as simple dilutions—see Table III. In these experiments, the change in concentration of PdI_4^{2-} was relatively large, up to 21%, but still strictly first-order rate plots were obtained. This is justified by the form of the integrated rate law for the reaction, eq 20.

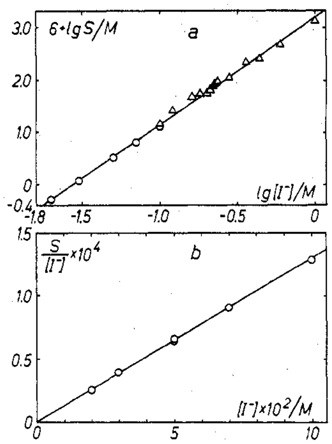

Figure 2. Solubility measurements: this investigation (○); Tananaev[2] (△); (a) log (S/M) vs. log ([I$^-$]/M); (b) S/[I$^-$] vs. [I$^-$] giving $K_{s4} + 2K_{s26} = (1.30 \pm 0.02) \times 10^{-3}$ M^{-1} as the slope.

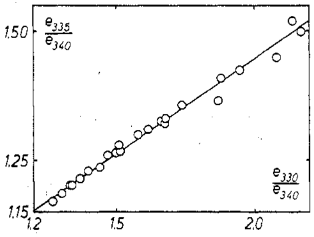

Figure 3. Equilibrium measurements: graphical test for the number of absorbing species according to Coleman et al.[14] Data are from Table I.

It was necessary to use supersaturated solutions to obtain measurable transmission changes. A slow precipitation of PdI_2(s) followed the observed reaction. Between successive experiments, the flow system had to be rinsed carefully with 0.3 M sodium iodide, followed by several portions of water in order to remove PdI_2(s) precipitates.

Results and Discussion

Stoichiometry and Equilibrium Constants. Figure 2a shows a plot of our solubility measurements and Tananaev's[2] previous results for the concentration interval $0.1 \leq [I^-] \leq 1$ M. The slope of the line, 2.05 ± 0.01, is equal to the average ionic charge of the predominant complexes—cf. ref 13, eq 10. Tananaev interpreted his results using the complex PdI_4^{2-} exclusively. However, it is obvious from the spectra shown in Figures 1a and b that polynuclear complexes are also present—the function $\epsilon_{Pd} = e/C_{Pd}$ varies with C_{Pd} for a constant concentration of iodide. Therefore, the solubility measurements should be described by formation of complexes with the stoichiometric composition $Pd_mI_{2m+2}^{2-}$ (m = 1, 2, ...). There is no deviation from the straight line for low iodide concentrations, so the percentage of complexes of the type $Pd_mI_{2m+1}^-$, for instance PdI_3^- and $Pd_2I_5^-$, must be rather small in the concentration range studied.

The graphical method of Coleman et al.[14] applied to the spectrophotometric equilibrium measurements in Table I indicated that only two absorbing species were present; cf. the linear plot in Figure 3. The data were refined using the least-squares minimizing program LETAGROP 4[15] and a UNIVAC 1108 computer. Complexes of varying composition were tried. The species PdI_4^{2-} and $Pd_2I_6^{2-}$ gave acceptable minima, in agreement with both the solubility measurements and the graphical test. However, U_{min}[15] decreased 30% if $PdI_3H_2O^-$ was included also, and the value of K_{26} decreased about 10%. Introduction of $Pd_2I_5H_2O^-$ gave no acceptable minimum. The following equilibrium constants and standard deviations were obtained: $K_{26} = 21 \pm 1$ M, $K_4 = 360 \pm 60$ M^{-1}. The value of K_4 should be considered with some caution. The standard deviation is rather large, since $PdI_3H_2O^-$ never amounts to more than about 4% of C_{Pd} in the concentration range used. The magnitude of the constant seems reasonable, however, if compared to the stepwise stability constants for $PdCl_4^{2-}$ (24 M^{-1}) and $PdBr_4^{2-}$ (163 M^{-1}).[1a]

We can now describe the solubility experiments using the following equilibria

$$PdI_2(s) + I^- + H_2O \rightleftarrows PdI_3H_2O^- \tag{5}$$

$$PdI_2(s) + 2I^- \rightleftarrows PdI_4^{2-} \tag{6}$$

$$2PdI_2(s) + 2I^- \rightleftarrows Pd_2I_6^{2-} \tag{7}$$

with the equilibrium constants

$$K_{s3} = [PdI_3H_2O^-]/[I^-] = K_{s4}/K_4 \tag{8}$$

$$K_{s4} = [PdI_4^{2-}]/[I^-]^2 \tag{9}$$

$$K_{s26} = [Pd_2I_6^{2-}]/[I^-]^2 = K_{s4}{}^2K_{26} \tag{10}$$

The solubility can be written

$$S = C_{Pd(sat)} = K_{s3}[I^-] + (K_{s4} + 2K_{s26})[I^-]^2 \tag{11}$$

The plot in Figure 2b of $S/[I^-]$ vs. $[I^-]$ gives zero intercept, within the experimental errors, which means that K_{s3} is too small to be determined in the concentration range used. The slope of the line is $K_{s4} + 2K_{s26} = K_{s4} + 2K_{s4}{}^2K_{26} = (1.30 \pm 0.02) \times 10^{-3}$ M^{-1} which gives $K_{s4} = (1.24 \pm 0.02) \times 10^{-3}$ M^{-1}. From eq 8 and 10 it follows that $K_{s3} = (3.4 \pm 0.8) \times 10^{-6}$ and $K_{s26} = (3.2 \pm 0.3) \times 10^{-5}$ M^{-1}. Obviously, the ratio $[Pd_2I_6^{2-}]/[PdI_4^{2-}] = K_{s26}/K_{s4} = 0.03$ will be independent of $[I^-]$ in saturated solutions. PdI_4^{2-} is the dominant species in the solubility study, and only about 6% of the palladium will be present as $Pd_2I_6^{2-}$ in the saturated solutions. So, the solubility is approximately equal to $[PdI_4^{2-}]$ as assumed by Tananaev.[2]

To conclude, the experiments demonstrate the existence of the complexes $Pd_2I_6^{2-}$ and PdI_4^{2-}. Small concentrations of $PdI_3H_2O^-$ are also probable in the concentration range used. There is no indication of PdI_5^{3-} or higher complexes. Such complexes should have been expected in our solutions, if Sundaram and Sandell's postulate of $PdCl_5^{3-}$ and $PdCl_6^{4-}$ in their early and often cited spectrophotometric study[16] was correct. However, it is easily shown that their experiments can be described by mononuclear complexes with coordination number 4 or less and the stability constants and molar absorptivities of ref 1a. So, as a matter of fact, their results give no evidence for the existence of $PdCl_5^{3-}$ or $PdCl_6^{4-}$.

Absorption Spectra. Figure 1c shows the absorption spectra for $Pd_2I_6^{2-}$ and PdI_4^{2-}. $Pd_2I_6^{2-}$ has a strong charge-transfer band at 3.00×10^4 cm^{-1} with ϵ_{26} 47 700 cm^{-1} M^{-1} and PdI_4^{2-} has two bands, one at 3.17×10^4 cm^{-1} with ϵ_4 17 000 cm^{-1} M^{-1} and the other at 2.45×10^4 cm^{-1} with ϵ_4 10 600 cm^{-1} M^{-1}. The spectrum for $Pd_2I_6^{2-}$ agrees satisfactorily with those reported[7,17] for $[N(C_2H_5)_4]_2[Pd_2I_6]$ in acetone. Spectra for PdI_4^{2-} seem to have been published only for $\lambda > 350$ nm,[18,19] where there is good agreement with our results. The spectra for PdI_4^{2-} and $Pd_2I_6^{2-}$ resemble those reported by Harris et al.[7] for the corresponding bromo complexes. The spectrum for I_3^- in Figure 1c agrees satisfactorily with that reported by Awtrey and Connick.[20]

Dissociation Kinetics. The experiments in Table II give the rate law

$$-d[Pd_2I_6^{2-}]/dt = k_{exptl}[Pd_2I_6^{2-}] \tag{12}$$

The observed rate constant, plotted vs. $[I^-]$ in Figure 4, can be expressed as a second-order polynomial

$$k_{exptl} = a' + b'[I^-] + c'[I^-]^2 \tag{13}$$

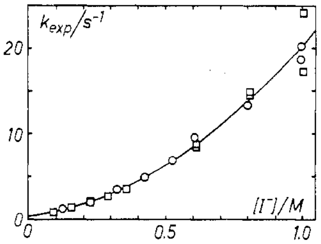

Figure 4. Dissociation kinetics: k_{exptl} vs. $[I^-]$. C_{Pd} was 1.55×10^{-5} (□) or 4.15×10^{-5} (○) M. The full-drawn curve was calculated from a', b', and c', according to eq 13.

with the parameters $a' = 0.42 \pm 0.09$ s^{-1}, $b' = 3.6 \pm 0.7$ s^{-1} M^{-1}, and $c' = 16.4 \pm 1.1$ s^{-1} M^{-2}.

For iodide concentrations greater than about 0.25 M, the reverse reaction, i.e., the formation of $Pd_2I_6^{2-}$, is completely suppressed, and $k_{exptl} = k_d$. For $[I^-] < 0.25$ M, the reverse reaction has a small influence on the overall kinetics, and k_d is slightly smaller than k_{exptl}; cf. Table II. The experiments indicate that the dissociation of $Pd_2I_6^{2-}$ follows the rate law

$$-d[Pd_2I_6^{2-}]/dt = k_d[Pd_2I_6^{2-}] \tag{14}$$

with k_d defined by

$$k_d = a + b[I^-] + c[I^-]^2 \tag{15}$$

where the parameters a, b, and c differ slightly from a', b', and c' (vide infra).

A simple kinetic experiment, in which the iodide concentration was kept constant (36 mM) and the palladium concentration was decreased to half of its initial value (2.32×10^{-5} M), gave a rate constant of 0.59 s^{-1} (cf. eq 13). This experiment demonstrates clearly that the observed kinetics must be due to a reaction of a polynuclear complex and not to the anation reaction (2), since the equilibrium quotient $[PdI_4^{2-}]/[PdI_3H_2O^-]$ remains constant, i.e., independent of C_{Pd}, as long as $[I^-]$ is not changed.

It is very unlikely that the observed second-order behavior in eq 13 and 15 is caused by a medium effect, since perchlorate and iodide ions in general seem to have an almost identical influence on other electrolytes in their aqueous solutions. For instance, solubility measurements by Nilsson[21] have shown that the activity factors are practically constant even if perchlorate is completely exchanged for iodide (cf. also Johansson[22]).

General Rate Law and Equilibrium Constant. Combining the rate law (eq 14) for the dissociation with the equilibrium expression (eq 3) gives a possible rate law for the case when both the forward and reverse reactions must be considered

$$d[Pd_2I_6^{2-}]/dt = k_f[PdI_4^{2-}]^2 - k_d[Pd_2I_6^{2-}] \tag{16}$$

Here, k_f should be expected to vary with the iodide concentration in the following manner

$$k_f = K_{26}c + K_{26}b/[I^-] + K_{26}a/[I^-]^2 \tag{17}$$

We can express the concentrations as

$$[Pd_2I_6^{2-}] = [Pd_2I_6^{2-}]_{eq} + x \tag{18}$$

$$[PdI_4^{2-}] = [PdI_4^{2-}]_{eq} - 2x \tag{19}$$

Substitution into eq 16 and integration give

$$\ln\{([PdI_4^{2-}]_{eq} + (k_d/4k_f) - x)/x\} = k_{exptl}t + \text{constant} \tag{20}$$

The concentration-jump experiments had $x << [PdI_4^{2-}]_{eq}$, and the dilution experiments (with a maximum conversion of PdI_4^{2-} of about 21%) had $x << [PdI_4^{2-}]_{eq} + (k_d/4k_f)$, so eq 20 gives

Table IV. Relaxation Experiments

$[I^-]$/mM	k_d^2/s^{-2}	$10^{-4}(8k_fk_d)$/ s^{-2} M^{-1}	K_{26}/M^a
	Concentration-Jump Experiments		
254	4.0 ± 0.9	2.6 ± 0.7	50 ± 30
100	0.84 ± 0.19	2.2 ± 0.4	33 ± 13
65.8	0.91 ± 0.05	1.17 ± 0.13	7 ± 1
49.8	0.20 ± 0.17	3.1 ± 0.6	(50 ± 50)
37.5	0.29 ± 0.05	3.0 ± 0.3	18 ± 5
30.4	0.03 ± 0.09	3.0 ± 0.5	(100 ± 200)
	Dilution Experiments		
50.8	0.55 ± 0.07	1.6 ± 0.2	10 ± 3
50.3	0.41 ± 0.14	1.6 ± 0.5	12 ± 8
20.03	0.15 ± 0.06	4.2 ± 0.6	14 ± 7

[a] Calculation of K_{26} from kinetics using plots of k_{exptl}^2 vs. C_{Pd} according to eq 23.

Table V. Relaxation Experiments

$[I^-]$/mM	k_d/s^{-1} ^{a}	$10^{-3}k_f/s^{-1}$ M^{-1} ^{a}
	Concentration-Jump Experiments	
254	2.19 ± 0.25	1.2 ± 0.5
100	0.98 ± 0.09	2.5 ± 0.5
65.8	0.94 ± 0.03	2.0 ± 0.2
49.8	0.49 ± 0.12	6.9 ± 1.4
37.5	0.54 ± 0.04	7.6 ± 0.7
30.4	0.30 ± 0.09	10.5 ± 1.6
	Dilution Experiments	
50.8	0.72 ± 0.04	3.6 ± 0.4
50.3	0.61 ± 0.09	4.2 ± 1.1
20.0	0.34 ± 0.06	19.1 ± 2.9

[a] Values of k_d and k_f obtained from linear plots of k_{exptl} vs. $[PdI_4^{2-}]_{eq}$ (values in Table III) according to eq 21.

first-order kinetics in all cases studied. The observed first-order rate constant is

$$k_{\mathrm{exptl}} = k_d + 4k_f[PdI_4^{2-}]_{eq} \qquad (21)$$

Introduction of

$$C_{\mathrm{Pd}} = [PdI_4^{2-}]_{eq} + 2[Pd_2I_6^{2-}]_{eq} \qquad (22)$$

($[PdI_3H_2O^-]$ can be neglected) and the equilibrium expression (eq 3) into eq 21 gives

$$k_{\mathrm{exptl}}^2 = k_d^2 + 8k_fk_dC_{\mathrm{Pd}} \qquad (23)$$

Hence, k_f and k_d can be determined from linear plots of k_{exptl}^2 vs. C_{Pd} for constant C_I using the values in Table III. The values of k_d and k_f obtained in that manner can be used to calculate the equilibrium constant K_{26} from eq 3; vide Table IV. Bearing in mind the large experimental uncertainties in the relaxation experiments the agreement between the calculated K_{26} values and the value 21 ± 1 M obtained from the equilibrium measurements is satisfactory and supports the rate law (eq 16) with k_d and k_f defined by eq 15 and 17.

It is now possible to calculate accurate values for the parameters *a*, *b*, and *c* in eq 15 from the dissociation experiments. Equations 3 and 23 give the following relation between k_{exptl} and k_d

$$k_d = k_{\mathrm{exptl}}/(1 + 8K_{26}C_{\mathrm{Pd}}/[I^-]^2)^{1/2} \qquad (24)$$

Table II contains the k_d values obtained from eq 24 with K_{26} = 21 M. A least-squares calculation using eq 15 gave a = 0.24 ± 0.07 s^{-1}, b = 4.3 ± 0.6 s^{-1} M^{-1}, and c = 15.5 ± 0.9 s^{-1} M^{-2}.

The K_{26} values calculated in Table IV from the relaxation experiments have large experimental errors. In Table III, we have therefore used K_{26} = 21 M and K_4 = 360 M^{-1} from the equilibrium measurements for calculation of $[PdI_4^{2-}]_{eq}$ in the relaxation experiments. Equation 21 can then be used for determination of more accurate values of k_d and k_f from linear plots of k_{exptl} vs. $[PdI_4^{2-}]_{eq}$. The values are given in Table V. Figure 5 shows plots of these k_d values vs. $[I^-]$ and k_f values vs. $1/[I^-]$ for the relaxation experiments. The full-drawn curves have been calculated from eq 15 and 17 using the parameters *a*, *b*, and *c* calculated above and K_{26} = 21 M. In view of the experimental uncertainties, the agreement between the relaxation experiments and the assumed rate law (15)–(17), demonstrated by the two plots in Figure 5, is satisfactory.

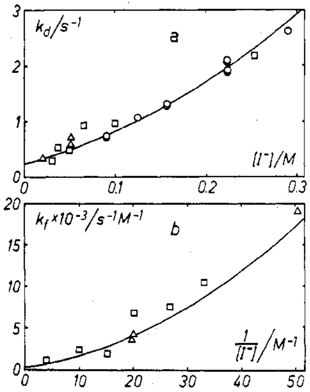

Figure 5. Relaxation kinetics: concentration-jump experiments (□) and dilution experiments (△) from Table V. For comparison, dissociation experiments from Table II have been included in part a (○). The curves were calculated from eq 15 and 17 with a = 0.24 s^{-1}, b = 4.3 s^{-1} M^{-1}, c = 15.5 s^{-1} M^{-2}, and K_{26} = 21 M.

Reaction Mechanism. The following stoichiometric mechanism with three parallel paths accounts for the three terms in the experimental rate law

$$PdI_3H_2O^- + I^- \rightleftarrows PdI_4^{2-} + H_2O \quad \text{fast} \qquad (25)$$

$$2PdI_4^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Pd_2I_6^{2-} + 2I^- \qquad (26)$$

$$PdI_4^{2-} + PdI_3H_2O^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Pd_2I_6^{2-} + I^- + H_2O \qquad (27)$$

$$2PdI_3H_2O^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} Pd_2I_6^{2-} + 2H_2O \qquad (28)$$

Reaction 25 can be considered as a fast preequilibrium in the present case because of the large concentrations of iodide used (cf. also the rate constants for the corresponding chloro and bromo complexes[1b]). Introducing the equilibrium constant K_4 for reaction 25 we get

$$\begin{aligned} d[Pd_2I_6^{2-}]/dt = {} & [PdI_4^{2-}]^2(k_1 + k_2K_4^{-1}[I^-]^{-1} + \\ & k_3K_4^{-2}[I^-]^{-2}) - [Pd_2I_6^{2-}](k_{-3} + k_{-2}[I^-] + \\ & k_{-1}[I^-]^2) \end{aligned} \qquad (29)$$

which agrees with the experimental eq 15, 16, and 17.

Each reaction path (26)–(28) might be visualized by the tentative mechanism in Figure 6. The first two stages A and B are identical with those proposed by Martin and coworkers[23,24] for the exchange of bromide ligands between dibromodiammineplatinum(II) and tetrabromoplatinate(II). The dimeric transition state with a double iodide bridge between the two palladium atoms might form for instance via the configuration C with two trigonal bipyramids having a common edge. The transition state might lose the two leaving ligands in two consecutive steps or in a concerted process (see below).

Pearson and Muir[27] and Muir and Cancio[28] have reported rate laws of the type

$$\text{rate} = (k_1 + k_2[Y])[\text{complex}] \qquad (30)$$

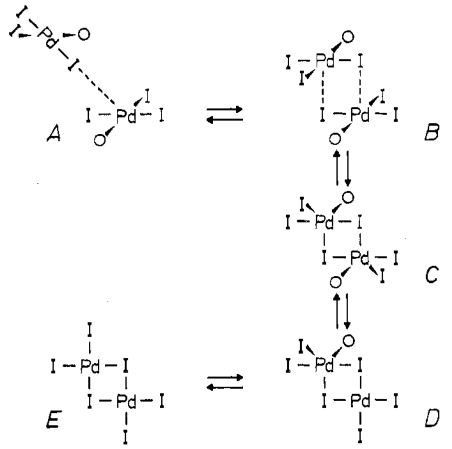

Figure 6. Possible reaction mechanism for formation/dissociation of $Pd_2I_6^{2-}$. ○ denotes leaving/entering ligand, i.e., H_2O or I^-.

for the cleavage of halogen-bridged complexes of platinum(II), for instance $Pt_2Br_6^{2-}$ and $Pt_2I_6^{2-}$, with amines and olefins as the entering nucleophile Y. Their results differ from ours in that no second-order dependence on the entering ligand was observed; compare eq 15 and 30. They suggested a mechanism with a rate-determining cleavage of the first bridge by Y or solvent, followed by a rapid cleavage of the second bridge, i.e.

$$M_2X_6^{2-} \underset{\text{slow}}{\overset{+Y}{\rightleftarrows}} -\underset{|}{\overset{|}{M}}-X-\underset{|}{\overset{|}{M}}- \underset{\text{fast}}{\overset{+Y}{\rightleftarrows}} 2MX_3Y^{2-} \qquad (31)$$

An analogous mechanism has been proposed by Martin and co-workers[25] to account for the exchange of bromide ligands in $PtBr_4^{2-}$. The rate law for this exchange contains a term which is proportional to the concentration product $[PtBr_4^{2-}][PtBr_3H_2O^-]$. This term is of the same form as the rate expression for the formation of $Pd_2I_6^{2-}$ from PdI_4^{2-} and $PdI_3H_2O^-$ according to reaction 27. The exchange was at least 100 times faster than the formation of $Pt_2Br_6^{2-}$, however, so the authors concluded that it occurred via a singly bridged dimeric species. $Pt_2Br_6^{2-}$ was assumed[26] to be formed from this singly bridged dimer by a slow subsequent closing of the second bromide bridge; cf. (31).

However, mechanism 31 cannot explain the second-order dependence on the entering ligand found in the present study nor can it account for the preference for symmetrical cleavage of dinuclear complexes observed both by Pearson and Muir[27,28] and by Chatt and Venanzi.[29] Therefore, a concerted process, in which the cleavage of the second bridge starts before the slow cleavage of the first bridge has been completed (path EDC in Figure 6) seems more likely. That was also suggested as a possibility by Pearson and Muir[27] to account for the symmetrical cleavage in their case.

Identification of the parameters in eq 29 with the experimental quantities gives $k_{-1} = c = 15.6 \pm 0.9$ s^{-1} M^{-2}, $k_{-2} = b = 4.2 \pm 0.6$ s^{-1} M^{-1}, $k_{-3} = a = 0.24 \pm 0.07$ s^{-1}, $k_1 = K_{26}c = (3.3 \pm 0.4) \times 10^2$ s^{-1} M^{-1}, $k_2 = K_4K_{26}b = (3.2 \pm 1.2) \times 10^4$ s^{-1} M^{-1}, and $k_3 = K_4^2K_{26}a = (7 \pm 4) \times 10^5$ s^{-1} M^{-1}. The rate constants for the forward reactions increase in the order $k_1 < k_2 < k_3$. One reason for this increase is the change in Coulombic repulsion between the charged reactants.

Acknowledgment. Our thanks are due to professor Ido Leden for valuable comments, to Miss Bodil Jönsson for experimental assistance, and to the Swedish Natural Science Research Council for financial support (Grant K 3650-002).

Registry No. PdI_2, 7790-38-7; $Pd_2I_6^{2-}$, 45513-78-8; PdI_4^{2-}, 16182-47-1; $PdI_3H_2O^-$, 63950-70-9.

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