data. Gladney and Swalen[20] have suggested electronic Raman and fluorescence experiments for this measurement. Magnetic resonance determinations of spin–lattice relaxation times should also provide information concerning the low-lying electronic states. These experiments will probably have to be carried out near 4.2°K. However, this work has shown that unusually high magnetic moments do not obtain in this series of hexafluorotitanates, and the results also demonstrate that unique sets of parameters Δ, λ, and k cannot be derived from the variation of magnetic susceptibilities in the range 300–77°K.

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CONTRIBUTION FROM HERCULES INC.,
WILMINGTON, DELAWARE 19899

Palladium(II) Chloride–Lithium Chloride Equilibria in Acetic Acid[1]

BY PATRICK M. HENRY* AND ORIN W. MARKS

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NaCl causes $PdCl_2$ to dissolve in acetic acid to give solutions with the composition $(NaPdCl_3)_n$. Molecular weight measurements indicate this material is a dimer, $Na_2Pd_2Cl_6$. Spectral measurements suggest that at low LiCl concentration the dimer $Li_2Pd_2Cl_6$ is also the main species. The extent of association of lithium chloride into dimers was also determined by molecular weight measurements. The value of K_D for the equilibrium

$$2LiCl \overset{K_D}{\rightleftarrows} Li_2Cl_2$$

was found to be 2.4 M^{-1} at 37.5°, close to the value previously reported at 16°. From an ultraviolet spectral study it was found that $Li_2Pd_2Cl_6$ reacts with lithium chloride according to the following equilibrium where K has a value of 0.1 M^{-1} at 25°

$$Li_2Pd_2Cl_6 + 2LiCl \overset{K}{\rightleftarrows} 2Li_2PdCl_4$$

Introduction

Recently the field of Pd(II) catalysis has received considerable attention as witnessed by the discovery of many new Pd(II)-catalyzed reactions.[2] The solvent used for a number of these new reactions is acetic acid. In spite of the importance of solvent acetic acid in Pd(II) catalysis, little is known about the state of Pd(II) salts in this solvent. This paper will describe equilibrium studies of the interaction of palladium(II) chloride with lithium chloride in acetic acid.

Experimental Section

Materials.—Palladium chloride (Engelhard Industries) was used without further purification. The acetic acid was dried by refluxing over $B(OOCCH_3)_3$.[3] The water content was less than 0.01% as determined by Karl Fischer. The lithium and sodium chlorides were of reagent grade.

Preparation and Analysis of Solutions.—The Pd(II) stock solutions were prepared by heating solid $PdCl_2$ in the presence of a solution of LiCl in acetic acid or, as in the case of the sodium system, with a mixture of solid NaCl and acetic acid. They were analyzed for Pd(II), chloride, and H_2O by standard procedures. LiCl stock solutions were prepared under carefully anhydrous conditions and analyzed for chloride and H_2O. They were used only if the water content was below 0.02%.

Pd(II) determinations were carried out by polarographic[4a] or by gravimetric[4b] analysis using dimethylglyoxime. Chloride analyses were usually carried out by the Volhard titration. With Pd(II)-containing solutions it was necessary to precipitate the Pd(II) with zinc to obtain accurate results.[4b] However, some were made using the Aminco-Cotlove coulometric chloride titrator made by the American Instrument Co.

Solutions for molecular weight measurements and ultraviolet spectral measurements were prepared by diluting stock solutions with anhydrous acetic acid.

Molecular Weights.—Originally molecular weights were measured by the Signer method[5] at 25°. However, this method did not prove sufficiently reproducible or accurate for our purposes. For the molecular weights reported in this paper the Mechrolab vapor pressure osmometer, Model 301A, was used. The preset temperature of the instrument for molecular weight measurement was 37.5°. The instrument was calibrated using urea solutions of known concentration in acetic acid.

Ultraviolet Spectral Study.—The spectra were run on a Cary Model 11 spectrometer at 25°. In order to obtain reproducible spectra, it was found necessary to ensure that the solutions were

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[1] Hercules Research Center Contribution No. 1521.

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dry. The cell thicknesses were 0.1, 1, and 10 mm depending on the Pd(II) concentrations.

A computer was used for the determination of uv absorption coefficients D_2 and D_1 of the ions $Li_2Pd_2Cl_6$ and Li_2PdCl_4 and equilibrium constants K_1 and K_D. Total uv absorbance D_i at several concentrations of chloride C_i can be used in a nonlinear regression routine[6] to obtain values for the parameters D_1, D_2, K_1, and K_D. One palladium concentration, Pd, and data for one wavelength are used for each computation of a set of parameters.

Let P_2 equal the amount of $Li_2Pd_2Cl_6$, P_1 the amount of Li_2PdCl_4, C_1 the amount of LiCl, and C_2 the amount of Li_2Cl_2. We can then write the material balance equations

$$2P_2 + P_1 = Pd \tag{1}$$

$$6P_2 + 4P_1 + 2C_2 + C_1 = C_i \tag{2}$$

and the equilibrium equations

$$K_1 = \frac{P_1^2}{P_2C_1^2} \tag{3}$$

$$K_D = \frac{C_2}{C_1^2} \tag{4}$$

Equations 2–4 can be combined with elimination of C_1 and C_2 to obtain

$$6P_2 + 4P_1 + 2P_1^2/(K_1P_2/K_D) + P_1/\sqrt{K_1P_2} - C_i = 0 \tag{5}$$

This is an equation in the unknown P_2 when we compute $P_1 = Pd - 2P_2$ from eq 1. It can be solved by an implicit method to obtain a value for P_2.

The predicted total absorbance is given by

$$\hat{D}_i = P_1D_1 - P_2D_2 \tag{6}$$

The nonlinear regression routine minimizes the sum of the squares of the deviations of these predicted D_i's from the observed D_i's.

Although the computer program was written to calculate K_D as a parameter, the data apparently were not good enough to warrant this. The regression routine failed to converge on most of the sets of data and widely different values for K_D were obtained on the few sets where convergence was obtained.

Similar computer programs were written to calculate the data, presuming that equilibria such as those represented by eq 9 and 10 are taking place. An example of the calculation of K_1 from one set of spectral data is shown in Table I.

TABLE I

EXAMPLE OF CALCULATION OF K_1 FROM SPECTRAL DATA[a]

[Cl], M	Absorbency[b] Calcd	Absorbency[b] Obsd	$10^2[Li_2Pd_2Cl_6]$,[c] M	$10^2[Li_2PdCl_4]$,[c] M	[LiCl],[c] M	$[Li_2Cl_2]$,[c] M	K_1,[c] M^{-1}
0.90	1.491	1.500	0.363	0.624	0.322	0.266	0.103
0.80	1.457	1.475	0.375	0.600	0.298	0.228	0.108
0.70	1.418	1.44	0.392	0.566	0.273	0.191	0.110
0.60	1.375	1.355	0.433	0.485	0.246	0.155	0.090
0.50	1.308	1.316	0.451	0.447	0.216	0.120	0.095
0.4	1.265	1.256	0.480	0.390	0.183	0.086	0.094
0.2	1.101	1.070	0.570	0.211	0.103	0.027	0.074
0.1	0.971	1.005	0.601	0.149	0.0468	0.0056	0.169

[a] $[Pd(II)]_t = 0.0135$ M; λ 280 nm; $K_D = 2.6$ M^{-1}. Best parameters: $K_1 = 0.0995$; $D_2 = 0.835$; $D_1 = 2.25$. [b] Standard deviation of absorbance 0.027. [c] Calculated by using the observed absorbance and best D_1 and D_2.

Results

State of Association of Palladium(II) Chloride at Low [LiCl].—Palladium(II) chloride is very insoluble in acetic acid alone, but addition of the soluble salt, LiCl, greatly increases the solubility and, by using a molar ratio of solid $PdCl_2$ to LiCl in solution of greater than 1, solutions can be made which contained close to three chlorides per Pd(II). If NaCl, which has low solubility in acetic acid, is used in place of LiCl, the solutions contain almost exactly three chlorides per Pd(II) as previously reported.[7] Thus, in these solutions, Pd(II) must exist as $(MPdCl_3)_n$ (M = Na or Li). The value of n was determined by molecular weight measurements. However, the measurement of n was complicated by the fact that the Pd(II) solutions contained excess LiCl or NaCl. This would cause the apparent molecular weights of $(MPdCl_3)_n$ to be low. If the concentration of LiCl or NaCl is known, the experimental molecular weight can be corrected to give the true molecular weight of $(MPdCl_3)_n$. In the lithium system if we assume that three chlorides are associated with Pd(II), the free lithium chloride concentration is then

$$[LiCl] = [Cl]_t - 3[Pd(II)]_t \tag{7}$$

where $[Cl]_t$ and $[Pd(II)]_t$ are the total Cl and Pd(II) concentrations obtained by analysis. In practice [LiCl] is the difference between two large numbers and difficult to obtain accurately. Furthermore, the molecular weight of $(LiPdCl_3)_n$ is very dependent on [LiCl]. In practice an error of 2% in $[Pd(II)]_t$ or 5% in $[Cl]_t$ can change the calculated value of the molecular weight of $(LiPdCl_3)_n$ by over 200. For example in one measurement $[Pd(II)]_t$ was 0.0388 M and $[Cl]_t$ was 0.131 M. The measured molecular weight was 338; by eq 7 [LiCl] was 0.015 M which gave a value of 730 for the molecular weight of $(LiPdCl)_n$. If $[Cl]_t$ were assumed to be 0.125 M, the molecular weight value became 476.

In order to overcome this difficulty, advantage was taken of the fact that NaCl has low solubility in acetic acid. The $(NaPdCl_3)_n$ stock solutions were prepared in the presence of excess NaCl and thus were saturated in NaCl. The solubility of NaCl in acetic acid at 37.5°, the temperature used for the molecular weight measurements, is 0.013 M.[8] The NaCl concentrations of the stock solutions used to make the solutions for molecular weight measurements are known and the experimental molecular weight can be corrected for the presence of NaCl. Results of molecular weight measurements are given in Table II. The average value of n in (NaPd-

TABLE II

MOLECULAR WEIGHT MEASUREMENTS ON $(NaPdCl_3)_n$ SOLUTIONS AT 37.5°

$[Pd(II)]_t$,[a] M	[NaCl],[b] M	Osmotic mol wt	n[c]
0.121	0.013	393	2.03
0.057	0.013	336	1.81
0.0437	0.0065	396	2.13
0.0303	0.00865	355	2.05
0.030	0.0065	354	2.22
0.017	0.0026	399	2.15
0.012	0.0026	314	1.82
		Av	2.03

[a] Total Pd(II) as found by analysis. [b] Calculated assuming [NaCl] = 0.013 M for stock solution used to prepare molecular weight solutions. [c] Calculated from the formula $\bar{M} = \{58.44 \cdot [NaCl] + 236.17[Pd(II)]_t\}/\{[NaCl] + ([Pd(II)]_t/n)\}$.

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$Cl_3)_n$ is very close to 2. Thus, in NaCl solutions Pd(II) exists as the dimer $Na_2Pd_2Cl_6$. In LiCl solutions at low [LiCl], Pd(II) would be expected to exist in the same form, and in fact, as shown below, there is ample evidence that it does.

Association of Lithium Chloride.—Lithium chloride is reported to associate to some extent to dimers in acetic acid.[9] The value of K_D for the dimerization was reported to be 2.8 M^{-1} from freezing point depression. To determine if K_D varies with temperature to any extent, molecular weight measurements were made on lithium chloride solutions at 37.5°. Some representative data are shown in Table III. The experimental molecular weight increases with $[Cl]_t$, indicating association. Since the value of K_D is very sensitive to both $[Cl]_t$ and experimental molecular weight, the variation in calculated K_D, also shown in Table III, is considerable. Thus a 5% error in $[Cl]_t$ or molecular weight at $[Cl]_t$ = 0.1 M causes a 40% error in K_D. For that reason $[Cl]_t$ and molecular weights were an average of two measurements. The average K_D from molecular weight measurements of 20 solutions gave a value of 2.4 M^{-1} with a standard deviation, σ, of 0.97. Thus K_D changes little with temperature. Since 25° is about halfway between 16 and 37.5°, a value of 2.6 for K_D was used in subsequent calculations.

TABLE III

VALUES OF K_D CALCULATED FROM MOLECULAR WEIGHT MEASUREMENTS ON LITHIUM CHLORIDE SOLUTIONS

$[Cl]_t$, M	Osmotic mol wt	[LiCl], M	$[(LiCl)_2]$, M	K_D, M^{-1}
0.0315	46.0	0.0267	0.0024	3.3
0.0525	46.5	0.0433	0.0046	2.4
0.0775	48.2	0.0587	0.0094	2.7
0.0935	49.1	0.0677	0.0129	2.8
0.133	49.2	0.0962	0.0184	2.0
0.1815	51.9	0.1151	0.0332	2.5

Pd(II)–LiCl Equilibrium in Acetic Acid.—The ultraviolet spectra of solutions of Pd(II) in anhydrous acetic acid, which are between about 0.025 and 0.8 M in lithium chloride, exhibit three isosbestic points. Sample spectra are shown in Figure 1. The presence of the isobestic points indicates that only two Pd(II) species are present in this range of chloride concentrations. At low chloride concentrations, the spectrum is identical with the spectrum of $Na_2Pd_2Cl_6$ saturated with NaCl strongly suggesting the starting species is the dimer, $Li_2Pd_2Cl_6$.

The data were treated by means of a nonlinear least-squares-fit regression analysis. Several types of equilibria were assumed and equilibrium constants were calculated. The various equilibria are shown in eq 8–10,

$$Li_2Pd_2Cl_6 + 2LiCl \overset{K_1}{\rightleftarrows} 2Li_2PdCl_4 \tag{8}$$

$$LiPdCl_3 + LiCl \overset{K_2}{\rightleftarrows} Li_2PdCl_4 \tag{9}$$

$$Li_2Pd_2Cl_6 + LiCl \overset{K_3}{\rightleftarrows} Li_3Pd_2Cl_7 \tag{10}$$

and the results are summarized in Table IV. Only for the equilibrium involving the reaction of dimer with two lithium chlorides (eq 8) were constant values of the equilibrium constant obtained at various $[Pd(II)]_t$'s and different wavelengths. The average value of the constant for a number of runs is 0.10 M^{-1}.

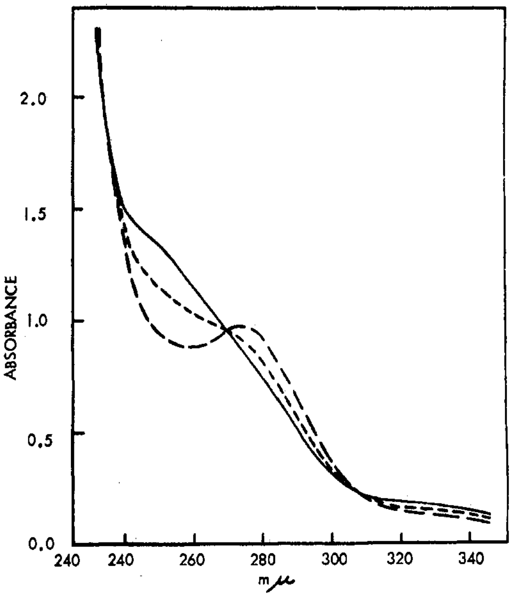


Figure 1.—Spectra of Pd(II) in acetic acid: ——, [LiCl] = 0.2 M; - - -, [LiCl] = 0.3 M; — —, [LiCl] = 0.5 M.

TABLE IV

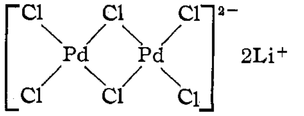
VALUES OF THE EQUILIBRIUM CONSTANTS FOR VARIOUS EQUILIBRIA[a]

$[Pd]_t$, M	λ, mμ	K_1, M^{-1}	K_2, M^{-1}	K_3, M^{-1}
0.00088	280	0.095	4.8	5.3
0.0045	255	0.13	4.6	5.6
0.01	275	0.10	1.1	0.43
0.01	255	0.11	2.4	2.6
0.0168	255	0.11	1.92	2.1

[a] $[Pd]_t$ constant and $[Cl]_t$ varied during a given run.

Discussion

The results clearly indicate that at low chloride concentration Pd(II) in acetic acid exists as a dimer. Almost certainly this dimer is the chloride-bridged dimer. X-Ray structures of similar Pd(II) structures have been determined[10,11] and there is considerable evidence that the chloride-bridged dimer type of structure exists in solvents of low dielectric constant.[12–14]



Furthermore the bridge-splitting reaction depicted by eq 8 is well known for Pd(II) chloro-bridged binuclear complexes.[13–15]

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The results of this study can be compared with the Pd(II)–Cl^- equilibrium in aqueous solution.[2b] In water there is no evidence for dimer and above a chloride concentration of 0.1 M the Pd(II) exists almost entirely as $PdCl_4^{2-}$. It is not surprising that in a low dielectric constant solvent, such as acetic acid, Pd(II) exists as a chloride-bridged dimer at low [LiCl] and that the equilibrium constant for breaking the dimer bridge is only 0.1 M^{-1}. However, it does mean that the study of Pd(II)-catalyzed reactions in acetic acid will be more complex than in water, first, because there will be more Pd(II) species to consider and, second, because there are several ways for a dimeric Pd(II) species to interact with a substrate. Furthermore, when lithium chloride is involved in the reaction sequence, the association of LiCl must be taken into account.

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A Kinetic Study of the Oxidation of the Tantalum Cluster Ion $Ta_6Br_{12}^{2+}$ by Chromium(VI)[1a]

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The oxidation of $Ta_6Br_{12}^{2+}$ to $Ta_6Br_{12}^{3+}$ by Cr(VI) occurs at a rate given by the expression $-d[Ta_6Br_{12}^{2+}]/dt = \{k_1 + k_2\cdot[HCrO_4^-]\}[H^+][HCrO_4^-][Ta_6Br_{12}^{2+}]$, with $k_1 = (9.53 \pm 0.25) \times 10^3\ M^{-2}\ sec^{-1}$ and $k_2 = (3.72 \pm 0.09) \times 10^7\ M^{-3}\ sec^{-1}$ (25.0°, $\mu = 1.00\ M$). The kinetic data for k_1 are consistent with a mechanism in which three successive single-electron steps convert Cr(VI) to Cr(III), by way of intermediate Cr(V) and Cr(IV). The kinetic data are also consistent with a two-electron mechanism, and no distinction is possible at present. The second rate term can be interpreted as a parallel oxidation by $Cr_2O_7^{2-}$. The corresponding value of k_1 for $Ta_6Cl_{12}^{2+}$ is $2.8 \times 10^4\ M^{-2}\ sec^{-1}$.

Introduction

Tantalum cluster ions $Ta_6X_{12}^{n+}$, with X = Br or C and n = 2, 3, or 4, have been shown to undergo reversible electron transfer,[2-4] and the mechanisms of some of their redox reactions have been considered.[4-6] The oxidation of $Ta_6Br_{12}^{2+}$ by $HCrO_4^-$ occurs according to the net equation

$$3Ta_6Br_{12}^{2+} + HCrO_4^- + 7H^+ = 3Ta_6Br_{12}^{3+} + Cr(III) + 4H_2O \qquad (1)$$

A consideration of the electrode potentials[3] indicates that further oxidation to the polynuclear 4+ ion should occur; that second step occurs more slowly, however, possibly accompanied by some decomposition of the cluster framework. The present work has been confined to a kinetic study of reaction 1 in acidic solution and to some related studies on $Ta_6Cl_{12}^{2+}$.

Experimental Section

The source of $Ta_6Br_{12}^{2+}$ is the hydrate salt $Ta_6Br_{14}\cdot 8H_2O$, prepared according to published procedures and purified by recrystallization from water.[2] Other reagents were prepared and purified as in earlier work.[7] The reaction kinetics were studied spectrophotometrically, using a Cary Model 14 instrument for most experiments,[7a] with a few experiments carried out using the stopped-flow method.[7b] In most of the rate runs the decrease in concentration of the $Ta_6Br_{12}^{2+}$ species was monitored using its intense absorption band at λ 637 nm (ϵ 7100 $M^{-1}\ cm^{-1}$), with a few runs performed at λ 870 nm, a maximum for the product $Ta_6Br_{12}^{3+}$ (ϵ ~6100 $M^{-1}\ cm^{-1}$). All the rate measurements were made at 25.0°, with lithium perchlorate added to maintain a constant ionic strength of 1.00 M.

Results and Interpretation

Stoichiometry.—The stoichiometry of the reaction was determined by spectrophotometric titrations of known amounts of $Ta_6Br_{12}^{2+}$ with $HCrO_4^-$. Breaks in the titration curves at $[Ta_6Br_{12}^{2+}]/[HCrO_4^-] = 3.0$ and 1.5 represent the two steps in the oxidation of $Ta_6Br_{12}^{2+}$ first to $Ta_6Br_{12}^{3+}$ and subsequently to $Ta_6Br_{12}^{4+}$.

The second reaction occurs much more slowly than the first, so that even with a considerable excess of $HCrO_4^-$, as was the case in the kinetic experiments described subsequently, no appreciable interference is caused by the reaction of the 3+ cluster ion and $HCrO_4^-$.

Kinetics.—In most kinetic experiments the concen-

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