

TABLE II

pH	$\epsilon_{p/2}$ (VOLTS)									
	$B_{10}H_{10}^{-2a}$	$B_{10}H_9OH^{-2}$	$B_{10}H_8(OH)_2^{-2}$	$B_{10}Cl_{10}^{-2b}$	$B_{10}Cl_9OH^{-2}$	$B_{10}Cl_8(OH)_2^{-2}$	$B_{12}H_{12}^{-2a}$	$B_{12}H_{11}OH^{-2}$	$B_{12}H_{10}(OH)_2^{-2}$	$B_{12}Br_{10}(OH)_2^{-2}$
4.5	+0.85	+0.60	+0.47	>+1.1	+1.03	+0.74	>+1.4	+0.98	+0.76	>+1.25
7	+0.85	+0.66	+0.62	>+1.1	+1.0	+0.70	>+1.4	.....	+0.77	.....
10	+0.85	+0.66	+0.63	>+1.1	+1.02	+0.68	>+1.4	.....	+0.74	.....

<sup>a</sup> See ref. 2. <sup>b</sup> See ref. 3.

iodide was added. The resulting precipitate was filtered and washed with hot water to leave  $B_{12}H_{10}[S(CH_3)_2]_2$ .

*Anal.* Calcd. for  $B_{12}H_{10}[S(CH_3)_2]_2$ : C, 18.1; H, 8.3; S, 24.2. Found: C, 17.8; H, 8.3; S, 24.2.

$B_{12}H_9(C_6H_9)_3^{-2}$ ,  $B_{12}H_{10}(C_6H_9)_2^{-2}$ , and  $B_{12}Cl_{10}(C_6H_9)_2^{-2}$ .—A solution of  $(H_3O)_2B_{12}H_{12} \cdot 5H_2O$  (5 g., 18.5 mmoles) and 5 ml. of 2-propanol was prepared at 0°. Styrene (5 g., 48 mmoles) was added and the temperature was maintained at 0–5° for 18 hr. and then at room temperature for 5 hr. (Under these conditions, 2-propanol alone does not react with  $(H_3O)_2B_{12}H_{12} \cdot 5H_2O$ .) Neutralization with cesium hydroxide precipitated  $Cs_2B_{12}H_9(C_6H_9)_3$  which was recrystallized from 50% aqueous 2-propanol (6.9 g., 52%).

*Anal.* Calcd. for  $Cs_2B_{12}H_9(C_6H_9)_3$ : B, 18.1; C, 40.0; H, 5.0. Found: B, 17.6; C, 41.6; H, 4.1.

In a similar experiment, a fraction was isolated from the recrystallization of the cesium salt which analyzed for a mixture of mono- and dialkylated  $B_{12}H_{12}^{-2}$  derivatives. The boron:styrene ratio was 12:1.4. Chlorination of this salt in acetonitrile at 25–40° gave a product with the same boron:styrene ratio and a boron:chlorine ratio of 12:10.6. A solution of hydrobromic acid (100 ml.) and 12 g. of the unchlorinated cesium salt with a boron:styrene ratio of 12:1.4 was distilled slowly over 3.5 hr., collecting 50 ml. of distillate. An oil separated from the distillate. This was separated, dried over potassium hydroxide pellets, and distilled. Ethylbenzene (1.0 g., 45%,  $n_D^{25}$  1.4908, b.p. 132°) was isolated. The infrared spectrum was identical with that of authentic ethylbenzene.

In another alkylation of  $(H_3O)_2B_{12}H_{12}$  (23 g., 85 mmoles) with styrene (15 g., 144 mmoles) in 2-propanol (18 ml.), the temperature during addition of the styrene was 8–12°. Subsequently, the mixture was stirred 4 hr. at 0–5° and 3 hr. at room temperature. It was then neutralized with 10% aqueous sodium hydroxide and steam distilled for 30 min. Precipitation of a cesium salt from the distillation residue with 50% aqueous cesium fluoride followed by recrystallization from water gave 28 g. (53%) of a salt analyzing for a 1:2  $Cs_2B_{12}H_{12}$ -styrene addition product.

*Anal.* Calcd. for  $Cs_2B_{12}H_{10}(C_6H_9)_2$ : B, 21.1; C, 31.2; H, 4.5. Found: B, 21.1; C, 32.2; H, 4.6.

Part of this product was converted to the corresponding tetramethylammonium salt by passage, in aqueous solution, through a sodium-charged cation-exchange column followed by precipitation of the tetramethylammonium salt from the effluent with tetramethylammonium hydroxide. This salt was then chlorinated in acetonitrile at 5 to 35° and recrystallized from water.

*Anal.* Calcd. for  $[(CH_3)_4N]_2B_{12}Cl_{10}(C_6H_9)_2$ : C, 34.1; H, 4.9; N, 3.2; Cl, 42.2. Found: C, 34.0; H, 4.4; N, 3.8; Cl, 42.6.

$B_{12}H_{11}(C_6H_9)_2^{-2}$  and  $B_{12}Cl_7H_4(C_6H_9)_2^{-2}$ .—A mixture of  $(H_3O)_2B_{12}H_{12} \cdot 5H_2O$  (15 g., 55 mmoles) and 30 g. of propylene was shaken under autogenous pressure at 35° for 48 hr. The crude product was dissolved in 10% aqueous sodium hydroxide and filtered. The addition of 50% aqueous cesium fluoride gave a gel-like precipitate which recrystallized from water to give 8.5 g. (37%) of  $Cs_2B_{12}H_{11}(C_6H_9)_2$ .

*Anal.* Calcd. for  $Cs_2B_{12}H_{11}(C_6H_9)_2$ : B, 28.8; C, 8.0; H, 4.0. Found: B, 27.5; C, 8.1; H, 4.2.

Chlorination of  $Cs_2B_{12}H_{11}(C_6H_9)_2$  in acetonitrile at 25–40° until no further chlorine was absorbed gave  $Cs_2B_{12}Cl_7H_4(C_6H_9)_2$ .

*Anal.* Calcd. for  $Cs_2B_{12}Cl_7H_4(C_6H_9)_2$ : C, 5.2; H, 1.6; Cl, 35.9. Found: C, 4.6; H, 1.6; Cl, 35.5.

**Polarographic Studies.**—The half-wave potentials ( $\epsilon_{p/2}$ ) shown in Table II were determined using a graphite-Nujol paste electrode *vs.* a saturated calomel electrode. The values at pH 4.5 were determined in 0.1 M  $KH_2PO_4$  and the studies at pH 7 and 10 were done using standard Britton-Robinson buffers. These values were determined at several concentrations and found to be essentially independent of concentration. The value of +0.47 for  $B_{10}H_8(OH)_2^{-2}$  at pH 4.5 is inconsistent with the values at pH 7 and 10. It may be that  $B_{10}H_8(OH)_2^{-2}$  is unstable at this pH because different values were obtained on rerunning the pH 4.5 solutions. In many cases, more than one oxidation peak was observed for these anions; only the first is reported.

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## The Rates and Mechanism of Substitution Reactions of Palladium(II)-Acetylacetonate Complexes

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The rates of some substitution reactions of palladium(II)-acetylacetonate complexes have been measured in 91% water–9% methanol. The reactions studied include acid hydrolysis, base hydrolysis, and halide substitution in acidic media. The order of nucleophile reactivity found is  $H_2O \approx OH^- < Cl^- < Br^- < I^- < SCN^-$ . The parallelism of this order of reactivity to that observed for platinum(II) complexes and the kinetic form of the observed rate constants suggest that palladium and platinum systems react by similar  $S_N2$  mechanisms. Because the leaving group is a chelate, the rate equation is a function of the hydrogen ion concentration and the concentration of added nucleophile. The role of hydrogen ion is to trap the half-open chelate ring.

The majority of the studies of the substitution reactions of planar complexes have dealt with Pt(II) systems.<sup>2</sup> The form of the observed rate constant

for most Pt(II) substitution reactions is

$$k_{\text{obsd}} = k_1 + k_2[X] \quad (1a)$$

where X is the entering nucleophile. The substitution reactions of Pt(II) complexes are interpreted in terms of a two-path mechanism in which the first-order rate constant  $k_1$  is associated with nucleophilic attack by the solvent, and the second-order rate constant  $k_2$  describes direct attack by the entering nucleophile.<sup>2</sup> The five-co-

(1) Sinclair Fellow 1960–1961, United States Rubber Fellow 1961–1962, Union Carbide Fellow 1962–1963.

(2) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 4; (b) R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787 (1960); (c) F. Basolo, H. B. Gray, and R. G. Pearson, *ibid.*, **82**, 4200 (1960); (d) H. B. Gray and R. J. Olecott, *Inorg. Chem.*, **1**, 481 (1962).

ordinate intermediate postulated may be stabilized by  $\pi$ -bonding.<sup>3</sup> The reactivity of various nucleophiles toward Pt(II) may be correlated with their *trans* effect<sup>4</sup> and the availability of vacant orbitals for back donation of electrons from Pt(II).

The mechanism postulated for Pt(II) reactions seems plausible as a general mechanism for all  $d^8$  planar complexes. A two-term rate law has been found for the substitution reactions of some Au(III) complexes.<sup>5</sup> The complexes of Ni(II), Pd(II), and Rh(I) are generally labile and have received less attention.<sup>6</sup> The present study of the substitution reactions of bis(acetylacetonate)palladium(II) was undertaken in an attempt to ascertain the generality of the substitution mechanism found for Pt(II). Further, it was hoped that the importance of  $\pi$ -bonding in determining nucleophilic reactivity toward Pd(II) could be estimated. The recent synthesis of thiocyanate linkage isomers with Pd(II)<sup>7</sup> indicates that  $\pi$ -bonding may be important in determining the structure and reactivity of palladium complexes.

### Experimental

**Materials.**—The complexes bis(acetylacetonato)palladium(II) and bis(acetylacetonato)platinum(II) were prepared as described in the literature<sup>8,9</sup> and characterized by analysis and infrared spectra. Dihalogeno(acetylacetonato)palladium(II) complexes were generated *in situ* by the reaction of the diaquo(acetylacetonato)palladium(II) cation with the appropriate anion. Reagent grade chemicals were used for the preparation of the reaction mixtures. Sodium hydroxide solutions were prepared from a stock solution of saturated NaOH and standardized against potassium biphthalate. The concentration of stock HCl and HClO<sub>4</sub> solutions was determined by titration against the standard NaOH. Stock solutions of the halide ions were prepared by weighing dried reagent grade salts and/or titration with silver nitrate. The Cu(NO<sub>3</sub>)<sub>2</sub> stock solutions were standardized by EDTA titration. Reagent grade anhydrous methanol was used without further purification. The final solutions used were 91% water by volume and 9% methanol, unless otherwise indicated.

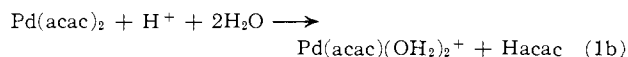
**Kinetic Studies.**—The rates of the substitution reactions were measured spectrophotometrically. Beckman DU, DK-2, and DB spectrophotometers were used to follow the change in absorbance with time. For the faster runs, a Beckman DU spectrophotometer, modified to accept a stopped flow mixing chamber by J. W. Moore,<sup>10</sup> was used. The majority of the reactions were followed with a Beckman DB linked to a Varian Model G11-A recorder. In a typical experiment, 2.0 ml. of the desired reaction medium was placed in a quartz cell of 1-cm. path length in a thermostated cell compartment. The reaction was started by adding 0.20 ml. of a methanol solution containing the complex. The hydrolysis and chloride substitution were measured at 322 m $\mu$ , the maximum of the starting material. The other substitution reactions were followed by observing the formation of the products in the near-visible region (Br<sup>-</sup>, 345–350; I<sup>-</sup>, 350–355; CNS<sup>-</sup>, 350–355 m $\mu$ ). The ionic strength of reaction mixtures was maintained with NaClO<sub>4</sub>.

Typically, the concentration of the complex was  $1-5 \times 10^{-5}$  M and the other reagents 0.001–0.500 M. Good first-order plots were obtained in most cases by plotting  $\log(A_t - A_\infty)$  vs. time. In

solutions of high pH, some difficulty was encountered in obtaining stable infinity values due to the cleavage of the acetylacetonate anion.<sup>11</sup> In these reactions the data were treated by the Guggenheim method.<sup>12</sup>

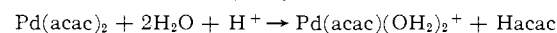
### Results

**Substitution Reactions in Acidic Solution.**—In perchloric acid solution, the spectrum of Pd(acac)<sub>2</sub> (acac<sup>-</sup> = acetylacetonate anion) disappears at a rate which is dependent upon the hydrogen ion concentration. From the equilibrium constants available in the literature,<sup>13</sup> the reaction taking place at moderate hydrogen ion concentration is expected to be



The change in the near-ultraviolet spectrum is consistent with this interpretation. The initial maximum at 322 m $\mu$  decreases with time and a new peak appears at 310 m $\mu$  with the same first-order rate. Figure 1 shows the initial and final spectra obtained. Table I

TABLE I  
OBSERVED RATE CONSTANTS FOR ACID HYDROLYSIS OF  
Pd(acac)<sub>2</sub> AT 25°



H <sup>+</sup> , M	<i>k</i> <sub>obsd</sub> × 10 <sup>2</sup> , sec. <sup>-1</sup> <sup>a</sup>	Comments <sup>b</sup>
0.051	0.84	<i>I</i> = 0.230
0.109	1.4	<i>I</i> = 0.230
0.145	1.6	<i>I</i> = 0.230
0.195	1.8	<i>I</i> = 0.230
0.230	2.0	<i>I</i> = 0.230
0.230	3.4	D <sub>2</sub> O–CH <sub>3</sub> OH, <i>I</i> = 0.230
0.300	2.3	<i>I</i> = 0.300
0.500	2.7	<i>I</i> = 0.500
0.162	1.7 (1.7)	Cu <sup>2+</sup> = 0.013 M
0.061	1.1 (0.96)	Cu <sup>2+</sup> = 0.038 M
0.061	1.4 (0.96)	Cu <sup>2+</sup> = 0.090 M
0.012	0.52 (0.25)	Cu <sup>2+</sup> = 0.038 M
0.012	1.1 (0.25)	Cu <sup>2+</sup> = 0.093 M
0.005	0.37 (0.11)	Cu <sup>2+</sup> = 0.066 M
0.005	0.23 (0.11)	Ni <sup>2+</sup> = 0.055 M

<sup>a</sup> The numbers in parentheses are in rate constants calculated for acid hydrolysis. <sup>b</sup> *I* refers to ionic strength.

summarizes the data obtained at various hydrogen ion concentrations. A plot of the observed rate constant vs. [H<sup>+</sup>] is shown in Fig. 2. The observed rate constant appears to be approaching a limiting value at the higher hydrogen ion concentrations used.

A plot of the inverse of the observed rate constant vs. the inverse of the hydrogen ion concentration is linear over the range of hydrogen ion concentrations used (Fig. 3). This suggests a rate constant for acid hydrolysis of the form

$$k_{\text{obsd}} = \frac{k_a[\text{H}^+]}{k_b + [\text{H}^+]} \quad (2)$$

The empirical values of *k*<sub>a</sub> and *k*<sub>b</sub> obtained from the slope and intercept of the plot shown in Fig. 3 are *k*<sub>a</sub> =  $3.2 \times 10^{-2}$  sec.<sup>-1</sup> and *k*<sub>b</sub> = 0.143 M.

Changing the solvent for hydrolysis from H<sub>2</sub>O–CH<sub>3</sub>OH to D<sub>2</sub>O–CH<sub>3</sub>OH causes an increase in the observed rate constant by a factor of 1.7. The observed

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(6) H. B. Gray and A. Wojcicki, *Proc. Chem. Soc.*, 358 (1960); F. Basolo and R. G. Pearson, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 3, H. J. Emeléus and A. G. Sharpe, Ed., Academic Press, New York, N. Y., 1961, p. 55.

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(10) To be described elsewhere.

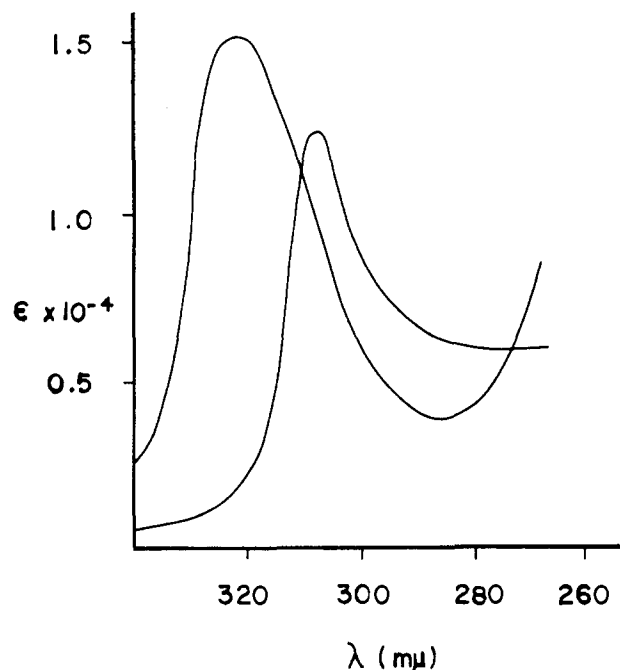


Fig. 1.—Spectral changes in acid hydrolysis of Pd(acac)<sub>2</sub>: higher curve, initial spectrum; lower curve, final spectrum.

rate constants are not greatly changed by varying the ionic strength of the reaction medium.

In solutions containing hydrohalic acids, or perchloric acid and sodium halides, the product of the reaction is the tetrahalogenopalladate(II) anion. The products of these reactions could be identified by their characteristic ultraviolet and visible spectra.<sup>14</sup> The rates of these substitution reactions were found to be dependent upon both the hydrogen ion and halide ion concentrations. At a fixed halide ion concentration, the observed rate constants show an acid dependence similar to that found for hydrolysis in perchloric acid solution. Holding the hydrogen ion concentration constant, the observed rate constant shows a linear dependence upon the halide ion concentration and a nonzero intercept at  $[X^-] = 0$  as shown in Fig. 4. The intercepts of these plots were found to agree within experimental error with the rate constant for acid hydrolysis. The data are consistent with an observed rate constant of the form

$$k_{\text{obsd}} = k' + k''[X^-] \quad (3)$$

where  $k'$  is the rate constant for acid hydrolysis and  $k'$  and  $k''$  are functions of  $[H^+]$ . The values of  $k''$  were found to increase in the order  $Cl^- < Br^- < I^- < SCN^-$ . The data for halide substitution are summarized in Table II. The rate of chloride ion substitution in DCl-D<sub>2</sub>O solution was found to be greater than that for HCl-H<sub>2</sub>O by a factor of 1.9. Increased methanol content slows down the rates of substitution.

If chloride ion is added to a solution containing Pd(acac)(OH)<sub>2</sub><sup>+</sup>, a new peak immediately appears at 290 m $\mu$ . The appearance of this peak is accompanied by a small shift in the peak associated with Pd(acac)(OH)<sub>2</sub><sup>+</sup>. This rapid initial change is followed by a slower reaction to form PdCl<sub>4</sub><sup>2-</sup>. The initial change in the spectrum is too large to be accounted for by the presence of

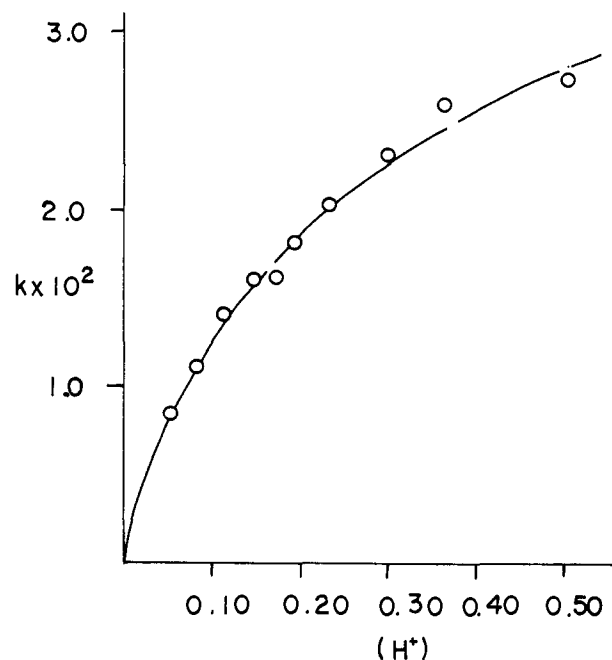


Fig. 2.—Plot of pseudo-first-order rate constant vs. hydrogen ion concentration in acid hydrolysis of Pd(acac)<sub>2</sub>.

TABLE II  
OBSERVED RATE CONSTANTS FOR HALIDE SUBSTITUTION  
REACTION, 25°

Pd(acac) <sub>2</sub> + 4X <sup>-</sup> + 2H <sup>+</sup> → PdX <sub>4</sub> <sup>2-</sup> + 2Hacac			
X <sup>-</sup>	H <sup>+</sup> , M	X <sup>-</sup> , M	k <sub>obsd</sub> × 10 <sup>2</sup> , sec. <sup>-1</sup>
Cl <sup>-</sup>	0.004	0.230 <sup>a</sup>	0.53
	0.023	0.230 <sup>a</sup>	1.2
	0.045	0.230 <sup>a</sup>	1.7
	0.091	0.230 <sup>a</sup>	2.7
	0.136	0.230 <sup>a</sup>	3.0
	0.186	0.230 <sup>a</sup>	3.7
	0.230	0.230 <sup>a</sup>	3.9
	0.002	0.045	0.13
	0.002	0.091	0.18
	0.002	0.160	0.25
	0.002	0.200	0.30
	0.230	0.000	2.0 <sup>b</sup>
	0.230	0.136	2.8
	0.230	0.165	3.0
	0.230	0.184	3.6
	0.230	0.230	3.9
0.0001	0.230	0.064 <sup>e</sup>	
0.0001	0.230	0.063 <sup>f</sup>	
0.0001	0.230	0.061 <sup>g</sup>	
Br <sup>-</sup>	0.023	0.000	0.45 <sup>b</sup>
	0.023	0.023	0.80
	0.023	0.068	1.80
	0.023	0.115	2.6
	0.115	0.000	1.4 <sup>b</sup>
	0.115	0.023	1.8
	0.115	0.068	3.3
	0.115	0.115	4.6
I <sup>-</sup>	0.065	0.040	1.6 <sup>c</sup>
	0.065	0.050	2.6 <sup>c</sup>
	0.144	0.041	3.2 <sup>c</sup>
	0.072	0.073	8.1 <sup>c</sup>
SCN <sup>-</sup>	0.086	0.082	6.6 <sup>d</sup>
	0.086	0.178	23.0 <sup>d</sup>
	0.086	0.030	20.0 <sup>d</sup>
	0.086	0.054	23.0 <sup>d</sup>
		0.165	51.0 <sup>d</sup>

<sup>a</sup> Ionic strength = 0.230. <sup>b</sup> Rate constant for acid hydrolysis. <sup>c</sup> T = 3°. <sup>d</sup> T = 25°, 40% CH<sub>3</sub>OH. <sup>e</sup> CH<sub>3</sub>CO<sub>2</sub>H = 0.02 M. <sup>f</sup> CH<sub>3</sub>CO<sub>2</sub>H = 0.05 M. <sup>g</sup> CH<sub>3</sub>CO<sub>2</sub>H = 0.65 M.

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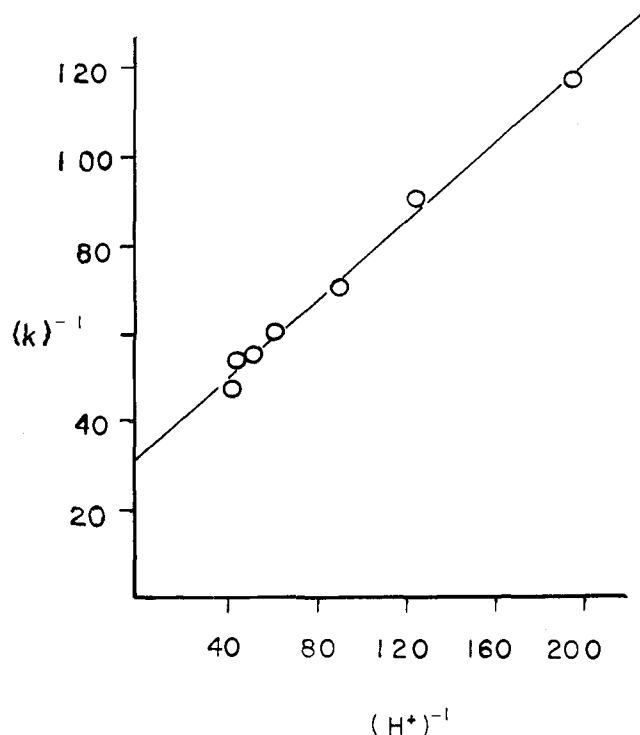


Fig. 3.—Plot of  $(k)^{-1}$  vs.  $(H^+)^{-1}$  in acid hydrolysis of  $Pd(acac)_2$ . small amounts of  $Pd(OH)_4^{2+}$ . It is assumed that the first change in the spectrum is due to the rapid formation of  $Pd(acac)Cl_2^-$ , followed by subsequent substitution by chloride to yield  $PdCl_4^{2-}$ . The first-order rate constants for substitution of some  $Pd(acac)(X)_2^-$  complexes are given in Table III and are seen to be several times faster than the substitution of  $X^-$  into  $Pd(acac)_2$ .

TABLE III

OBSERVED RATE CONSTANTS FOR THE SUBSTITUTION REACTIONS OF DIHALO(ACETYLACETONATO)PALLADIUM(II) COMPLEXES, 25°

$Pd(acac)X_2^- + 2X^- + H^+ \longrightarrow PdX_4^{2-} + Hacac$			
$X^-$	$H^+, M$	$X^-, M$	$k_{obsd} \times 10^2, sec.^{-1}$
Cl <sup>-</sup>	0.080	0.150	6.5 <sup>a</sup>
	0.165	0.150	7.4 <sup>a</sup>
	0.240	0.150	8.8 <sup>a</sup>
	0.240	0.050	6.3 <sup>a</sup>
	0.240	0.100	7.4 <sup>a</sup>
Br <sup>-</sup>	0.125 <sup>b</sup>	0.025	53 <sup>a</sup>
	0.125 <sup>b</sup>	0.096	77 <sup>d</sup>
	0.125 <sup>b</sup>	0.100	74 <sup>a</sup>
	0.125 <sup>b</sup>	0.125	100 <sup>c</sup>
	0.125 <sup>b</sup>	0.206	120 <sup>d</sup>
I <sup>-</sup>	0.050 <sup>b</sup>	0.082	64 <sup>c</sup>
	0.050 <sup>b</sup>	0.200	81 <sup>c</sup>
	0.138 <sup>b</sup>	0.13	110 <sup>c</sup>
	0.138 <sup>b</sup>	0.18	170 <sup>c</sup>

<sup>a</sup>  $I = 0.240$ . <sup>b</sup> Stopped flow technique used. <sup>c</sup>  $I = 0.250$ . <sup>d</sup>  $I = 0.375$ .

**Base Hydrolysis of  $Pd(acac)_2$ .**—In solutions of moderately high hydroxide ion concentration (0.05–0.500  $M$ ),  $Pd(acac)_2$  reacts to generate the anion of acetylacetonate and a soluble palladium species. The formula of the palladium product is not known; however,  $Pd(OH)_4^{2-}$  has been suggested as the species present in solutions of high pH.<sup>15</sup> The rate of base hydrolysis of  $Pd(acac)_2$  was measured at a number of

(15) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York, N. Y., 1962, p. 287.

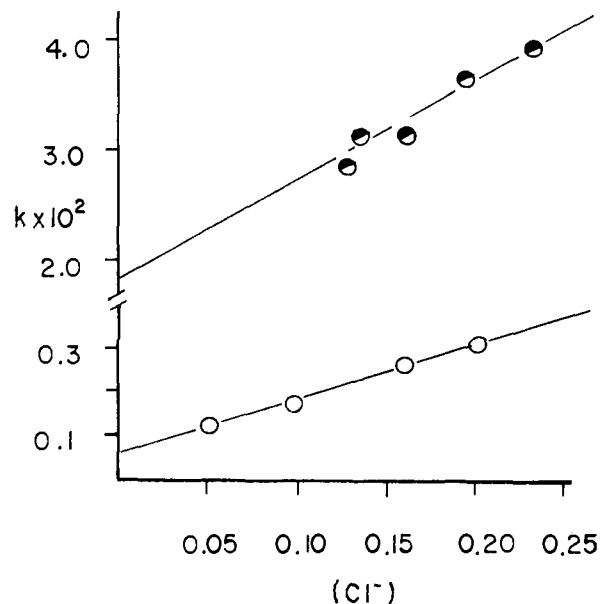


Fig. 4.—Dependence of observed first-order constants on chloride ion concentration in the reaction  $Pd(acac)_2 + 4HCl \rightarrow PdCl_4^{2-} + 2Hacac + 2H^+$ : upper curve 0.23  $M H^+$ ; lower curve 0.002  $M H^+$ .

hydroxide ion concentrations. The rate of base hydrolysis was found to be independent of the concentration of added nucleophiles such as  $Br^-$ . In  $D_2O$ , the rate of base hydrolysis is increased by a factor of 2.9.

The observed first-order rate constants for base hydrolysis are compiled in Table IV. Good isobestic points were observed for 80–90% of the reaction. Near the end of the reaction, the isobestic points are lost, presumably due to cleavage of the acetylacetonate anion. A plot of  $k_{obsd}$  vs.  $[OH^-]$  is nearly linear with some curvature at the higher concentrations. A plot of the inverse of the observed rate constant vs. the inverse of the hydroxide ion concentration is linear and gives the same intercept as a similar plot for acid hydrolysis within experimental error.

TABLE IV

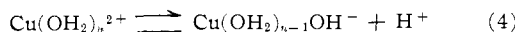
OBSERVED RATE CONSTANTS FOR BASE HYDROLYSIS OF  $Pd(acac)_2$ , 25°

$Pd(acac)_2 + 4OH^- \longrightarrow Pd(OH)_4^{2-} + 2acac^-$	
$OH^-, M$	$k_{obsd} \times 10^3, sec.^{-1}$
0.050	0.35 <sup>a</sup>
0.062	0.70 <sup>b</sup>
0.125	1.5 <sup>b</sup>
0.180	1.8 <sup>c</sup>
0.196	1.9 <sup>b</sup>
0.206	2.1 <sup>a</sup>
0.230	2.3 <sup>b</sup>
0.300	2.9 <sup>a</sup>
0.300	3.2 <sup>d</sup>
0.380	3.4 <sup>a</sup>
0.400	3.8 <sup>e</sup>
0.500	4.6 <sup>g</sup>
0.500	13.0 <sup>f</sup>

<sup>a</sup>  $I = 0.500$ . <sup>b</sup>  $I = 0.230$ . <sup>c</sup>  $I = 0.500$ ,  $Cl^- = 0.320 M$ . <sup>d</sup>  $I = 0.500$ ,  $Br^- = 0.200 M$ . <sup>e</sup>  $I = 0.500$ ,  $Br^- = 0.100 M$ . <sup>f</sup>  $I = 0.500$  in  $D_2O-CH_3OH$ .

**Metal Ion Catalyzed Hydrolysis.**—In the presence of metal ions such as  $Cu^{2+}$ ,  $Pd(acac)_2$  hydrolyzes at a rate which is dependent upon the concentration of metal ion present. Rate constants for the hydrolysis of  $Pd(acac)_2$  in the presence of  $Cu^{2+}$  are given in Table I.

The increased rates of hydrolysis are too large to be accounted for on the basis of the dissociation of the aquo ion.

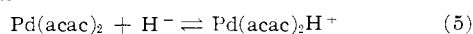


Nickel(II) salts are less effective as catalysts (Table I).

Acetic acid-sodium acetate buffers were used in an attempt to differentiate between general and specific acid catalysis. The rate of the chloride ion reaction was found to be independent of the concentration of added acetic acid and slightly higher than calculated for the pH range in which the experiments were carried out.

### Discussion

The observed nonlinear dependence of the rates on hydrogen ion concentration could be due to an acid-base pre-equilibrium.



The assumption would be that the protonated complex is more labile than the free complex. The limiting rate apparently reached at high hydrogen ion concentration would be due to complete protonation.

Several kinds of evidence argue against this interpretation. One is that the limiting rate would be expected to be reached at the same hydrogen ion concentration no matter what nucleophile reacted. This is not the case as described later. Another kind of evidence against preprotonation involves attempts to observe a change in the ultraviolet spectrum upon protonation. Extrapolation to zero time of the observed absorbance for a number of reactions at various hydrogen ion concentrations yielded the same initial value for the same concentration of  $\text{Pd}(\text{acac})_2$ . To avoid the problem of extrapolating to zero time,  $\text{Pt}(\text{acac})_2$  was also used as a model system for the protonation of the palladium complex. It was found that the spectrum of  $\text{Pt}(\text{acac})_2$  in perchloric acid solutions did not change with time. Within experimental error, the spectrum of  $\text{Pt}(\text{acac})_2$  in the region 340–250  $m\mu$  is independent of the acid concentration. Apparently acid hydrolysis of  $\text{Pt}(\text{acac})_2$  is either very slow or does not occur because of an unfavorable equilibrium constant. It was found that  $\text{Pt}(\text{acac})_2$  did react in these solutions when exposed to light; however, the products of the reaction have not been fully identified. It has been assumed that the basicities of  $\text{Pt}(\text{acac})_2$  and  $\text{Pd}(\text{acac})_2$  are similar. To the extent that this approximation holds, these experiments suggest that very little protonation of these complexes takes place even at the highest hydrogen ion concentration used.

An alternative mechanism involves an initial displacement of one end of the chelate ring by the entering nucleophile. The half-bonded complex may reclose to form the starting material or react with a proton to form a species which would lead to product formation.<sup>16</sup> This mechanism for acid hydrolysis is represented on the left-hand side of Fig. 5. In the absence of an added nucleophile, assuming a stationary state for the concentration of intermediates I' and II', the predicted form of the rate constant would be

$$k_{\text{obsd}} = \frac{k_1 k_2 K [\text{H}^+]}{k_{-1} + k_2 K_1 [\text{H}^+]} = \frac{k_1 [\text{H}^+]}{\frac{k_{-1}}{k_2 K_1} + [\text{H}^+]} \quad (6)$$

(16) Such a mechanism was first proposed for  $\text{Fe}(\text{bipy})_2^{2+}$  by F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, **75**, 5102 (1953).

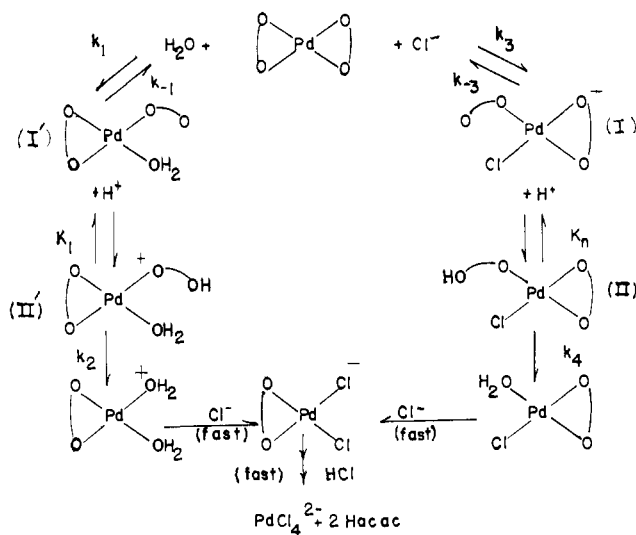


Fig. 5.—Mechanism for the substitution reactions of  $\text{Pd}(\text{acac})_2$ .

### Inverting

$$(k_{\text{obsd}})^{-1} = (k_1)^{-1} + \frac{k_{-1}}{k_1 k_2 K_1} [\text{H}^+]^{-1} \quad (7)$$

It can be seen that the linear requirement for  $(k_{\text{obsd}})^{-1}$  vs.  $[\text{H}^+]^{-1}$  is obeyed for this mechanism. The reaction of the half-bonded structure with a proton has been written as an equilibrium assuming the most likely site for protonation to be the chelate oxygen.

The extension of the displacement mechanism to the substitution reactions of other nucleophiles can be made by considering the observation that the reaction of the diaquoacetylacetonatopalladium(II) cation with added nucleophiles is fast. This suggests that the slow step in the substitution of halide into  $\text{Pd}(\text{acac})_2$  is the formation of  $\text{Pd}(\text{acac})(\text{X})_2^-$  (where  $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ , etc.). The dihalogeno complex will be formed both by direct substitution and by reaction of halide ions with the diaquo complex. The right-hand side of Fig. 5 shows the details. For this mechanism the observed rate constant would have the form

$$k_{\text{obsd}} = \frac{k_1 [\text{H}^+]}{\frac{k_{-1}}{k_2 K_1} + [\text{H}^+]} + \frac{k_3 [\text{H}^+][\text{X}^-]}{k_1 K_n + [\text{H}^+]} \quad (8)$$

The values of  $k_3$  for various nucleophiles will be a measure of their reactivity toward the palladium complex used. The assumption that the protonation step is an equilibrium reaction is supported by the increase in rate when  $\text{D}_2\text{O}$  is substituted for  $\text{H}_2\text{O}$  in the solvent. A shift of the equilibrium would be expected in favor of the protonated complex.<sup>17</sup> A similar equilibrium shift would be expected for the pre-equilibrium protonation mechanism discussed above; however, the form of the observed rate constant for the halide substitution reactions for this mechanism would be

$$k_{\text{obsd}} = \frac{k_1 [\text{H}^+]}{K_b + [\text{H}^+]} + \frac{k_3 [\text{X}^-][\text{H}^+]}{K_b + [\text{H}^+]} \quad (9)$$

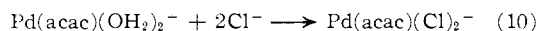
where  $K_b$  is the equilibrium constant for reaction 5. Experimentally it is found that the values of the con-

(17) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp. 187–188.

stant terms in the denominators of the hydrolysis and substitution terms differ by a factor of ten. The displacement mechanism seems to best fit the experimental data.

The ability of metal ions such as  $\text{Cu}^{2+}$  to catalyze these reactions also supports the displacement mechanism. The function of the metal ion is apparently to trap the opened chelate and decrease the possibility of reclosure of the ring. The details of the mechanism for this reaction are not known; however, it is assumed that the free end of the chelate assumes a position in the first coordination sphere of the metal ion. The use of metal ions to catalyze chelate uncoiling reactions has been previously reported.<sup>18</sup>

The substitution reactions of the dihaloacetylacetonatopalladium(II) complexes appear to be similar to those of the bisacetylacetonate. Attempts to measure the rate of the reaction



were unsuccessful. The half-life of this reaction has been estimated to be of the order of 1 msec. The rates of the subsequent substitution reactions were measured using the stopped-flow technique. The data are given in Table III and are incomplete; however, it appears that a mechanism similar to that proposed for the substitution of  $\text{X}^-$  into  $\text{Pd}(\text{acac})_2$  will explain the results.

The experimental data for the halide substitution reactions of  $\text{Pd}(\text{acac})_2$  have been analyzed in two ways. First, the contribution due to the solvent path was calculated from the data for acid hydrolysis and this contribution subtracted from the rates of substitution. A plot of the inverse of this corrected rate constant *vs.*  $[\text{H}^+]^{-1}$  is linear, and from the slope and intercept one may obtain  $k_3$  and  $(k_{-3}/k_4K_n)$ . An independent method of analysis involves data for the observed rates of substitution for fixed  $[\text{H}^+]$  and variable nucleophile concentration. Reference to eq. 8 shows that slope of a plot  $k_{\text{obsd}}$  *vs.*  $[\text{X}^-]$  will be

$$\text{slope} = \frac{k_3[\text{H}^+]}{k_{-3}/k_4K_n + [\text{H}^+]} \quad (11)$$

From the slopes of two such plots, for different  $[\text{H}^+]$ , the values of  $k_3$  and  $(k_{-3}/k_4K_n)$  may be obtained. The values of the parameters for chloride ion obtained by these two procedures are in good agreement. The rate parameters determined in this way for halide substitution are summarized in Table V. The order of

TABLE V  
SUMMARY OF RATE PARAMETERS FOR THE SUBSTITUTION REACTIONS OF  $\text{Pd}(\text{acac})_2$

X	$k_3$	$k_{-3}/k_4K_n$
$\text{H}_2\text{O}$	$3.2 \times 10^{-2} \text{ sec.}^{-1}$ <sup>a</sup>	0.143 <sup>b</sup>
$\text{OH}^-$	$3.2 \times 10^{-2} \text{ sec.}^{-1}$	2.90 <sup>c</sup>
$\text{Cl}^-$	$8.9 \times 10^{-2} M^{-1} \text{ sec.}^{-1}$	0.018
$\text{Br}^-$	$32.0 \times 10^{-2} M^{-1} \text{ sec.}^{-1}$	0.017
$\text{I}^-$	Fast	
$\text{SCN}^-$	Very fast	

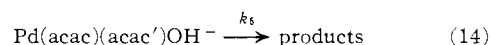
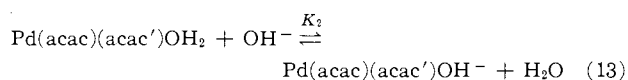
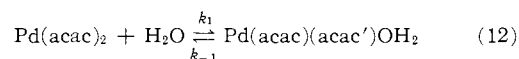
<sup>a</sup>  $k_1$  in Fig. 5. <sup>b</sup>  $k_{-1}/k_2K_1$ . <sup>c</sup>  $k_{-1}/k_3K_2$  where  $K_2$  is the equilibrium constant for reaction 13 and  $k_3$  is the rate constant for the further dissociation of  $\text{Pd}(\text{acac})(\text{acac}')\text{OH}^-$ .

(18) F. Basolo and R. G. Pearson, ref. 2a, p. 199, R. W. Taft, Jr., and E. H. Cook, *J. Am. Chem. Soc.*, **81**, 46 (1959); T. J. Bydalek and D. W. Margerum, *ibid.*, **83**, 4362 (1961); *Inorg. Chem.*, **1**, 852 (1962); *ibid.*, **2**, 678 (1963).

increasing reactivity toward this  $\text{Pd}(\text{II})$  complex parallels that found for  $\text{Pt}(\text{II})$ <sup>2c,d</sup> (estimates of the relative reactivity of  $\text{I}^-$  and  $\text{SCN}^-$  are made on the basis of experiments at low temperatures and in solutions of higher methanol concentration).

The data for the substitution of halide ions into  $\text{Pd}(\text{acac})(\text{X}_2)^-$  have some application to the determination of the relative *trans* effect of various halides toward  $\text{Pd}(\text{II})$ . On electrostatic grounds, it might be expected that the substitution of  $\text{X}^-$  into the negatively charged dihalo ions would be slower than that observed for the neutral  $\text{Pd}(\text{acac})_2$ . However, the second step of the reaction has been found to be faster than the first step. This indicates that the *trans* effect of these ligands is sufficient to overcome the electrostatic repulsion. A direct comparison of the relative *trans* effects of  $\text{Cl}^-$  and  $\text{Br}^-$  may be obtained by comparing the data obtaining for substitution reactions at the same hydrogen ion concentration. Extrapolation of the observed rates of substitution to  $[\text{X}^-] = 0$  gives a nonzero intercept in each case. The intercept of these plots will refer to the solvent path for the two complexes  $\text{Pd}(\text{acac})(\text{Cl})_2^-$  and  $\text{Pd}(\text{acac})(\text{Br})_2^-$ . It is found that the intercept for  $\text{Br}^-$  is an order of magnitude greater than that for  $\text{Cl}^-$ ; hence  $\text{Br}^-$  has a larger *trans* effect than  $\text{Cl}^-$ , the same as for  $\text{Pt}(\text{II})$ .

The rates of base hydrolysis of  $\text{Pd}(\text{acac})_2$  may be explained by assuming that the initial step in the reaction is nucleophilic attack by a solvent molecule followed by a rapid reaction with hydroxide ion to form a hydroxy complex by a simple proton transfer.



(The symbol  $\text{acac}'$  represents the half-bonded acetylacetonate group)

This mechanism leads to a limiting rate constant at infinite  $[\text{OH}^-]$  which is equal to  $k_1$ . This is exactly what is found in the reciprocal rate constant-concentration plots, since the rate constant for water substitution found for base hydrolysis is the same as that for acid hydrolysis within experimental error. Another way to check is to notice that even at 0.50 *M* hydroxide ion, the observed pseudo-first-order rate constant  $1.3 \times 10^{-2} \text{ sec.}^{-1}$  (Table IV) is less than the value of  $k_1$  for water,  $3.2 \times 10^{-2}$  (Table V).

An examination of the right-hand side of Fig. 5 shows that the halide substitution path will not operate efficiently in basic solution. Thus no proton transfer can occur to remove intermediate I in the same way that intermediate I' is removed. This predicts that nucleophiles such as bromide ion will have little effect on the over-all rate of disappearance of  $\text{Pd}(\text{acac})_2$  in basic solution. This is the observed result as shown in Table IV.

The solvent isotope effect (increased rate by a factor of 2.9 in  $\text{D}_2\text{O}$  compared to  $\text{H}_2\text{O}$ ) is in agreement with theory. The equilibrium constant for reaction 13 will be greater in  $\text{D}_2\text{O}$  than in  $\text{H}_2\text{O}$  because of the large

isotope effect in the autoprotolysis constant of water ( $K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}} = 6.5^{19}$ ).

### Conclusions

The similarity of Pd(II) to Pt(II) which is seen in the discussion above implies that the mechanism of Pd(II) substitution reactions is the same as for Pt(II), at least in the gross features. Edwards and Pearson<sup>20</sup> have discussed a model for nucleophilic reactivities in terms of the basicity and polarizability of the entering nucleophile. Analysis of the data for Pt(II) has led to the observation that the dominant feature is polarizability. For Pd(II) the increasing rates of substitution  $\text{H}_2\text{O} < \text{Cl}^- < \text{Br}^- < \text{I}^- < \text{SCN}^-$  suggest that polarizability is also the important factor in determining nucleophilic reactivity. For Pt(dien)Br<sup>+</sup> the relative reactivities are given as  $1:2 \times 10^3:1 \times 10^4$  for  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$ . For Pd(acac)<sub>2</sub>, the relative reactivities are  $1:1.5 \times 10^2:4 \times 10^2$ . For both Pt(II) and Pd(II), hydroxide ion is a poor nucleophile.

It is interesting to compare the data for the relative *trans* effect of  $\text{Cl}^-$  and  $\text{Br}^-$  in Pt(II) to that estimated for Pd(II) in this work. For Pt(II), the relative *trans* effect of  $\text{Br}^-$  vs.  $\text{Cl}^-$  shows a threefold increase in the rate of *trans* substitution.<sup>21</sup> For Pd(acac)X<sub>2</sub> the relative *trans* effect of  $\text{Br}^-$  vs.  $\text{Cl}^-$  is estimated to be 10:1.

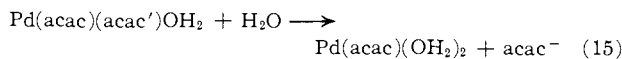
(19) R. W. Kinglerley and V. K. La Mer, *J. Am. Chem. Soc.*, **63**, 3256 (1941).

(20) J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

(21) O. E. Zvyagintsev and E. F. Karandasheva, *Dokl. Akad. Nauk SSSR*, **101**, 93 (1955).

This larger ratio is somewhat surprising. Earlier, very fragmentary evidence<sup>4</sup> suggested that while a *trans* effect existed for palladium(II), it was of less importance than in the case of platinum(II).

The data of Table I and particularly Table II, where lower concentrations of hydrogen ion could be used, show that the rate of dissociation of Pd(acac)<sub>2</sub> goes to zero as  $[\text{H}^+]$  goes to zero. Table IV shows also that the rate goes to zero as  $[\text{OH}^-]$  goes to zero. Thus the dissociation of the intermediate I'



has a negligible rate compared to the reclosing of the chelate ring governed by  $k_{-1}$ . It is precisely this ratio of the rate of closing of the ring compared to dissociation which creates the extra stability of a chelate ligand compared to a unidentate ligand.<sup>22</sup> For other bidentate chelates such as ethylenediamine and glycine, this ratio is about 20–30.<sup>23</sup> The corresponding ratio for the anion of acetylacetonate must be greater than 100. Consequently, a very large chelate effect exists.

**Acknowledgment.**—This work was supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-1087. The authors are indebted to Professor F. Basolo and Mr. John Moore for valuable aid.

(22) See ref. 2a, p. 18, for a discussion of the chelate effect.

(23) A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 2901 (1960); G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN, AND THE UNIVERSITY OF COLORADO, BOULDER, COLORADO]

## The Solvation of Chromium(III) Ion in Acidic Water–Methanol Mixed Solvents<sup>1,2</sup>

BY JERROLD C. JAYNE AND EDWARD L. KING<sup>3</sup>

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The low rate of exchange of solvent molecules between the first coordination shell of solvated chromium(III) ion and the solvent allows evaluation of  $\bar{n}$ , the average number of methanol molecules bound per chromium(III) ion, as a function of solvent composition in acidic water–methanol solutions. The data indicate that with respect to first shell coordination chromium(III) ion discriminates in favor of water over methanol. At 60°,  $\bar{n}$  ranges from 0.17 at  $Z_{\text{MeOH}} = 0.155$  to 3.60 at  $Z_{\text{MeOH}} = 0.98$ . (The mole fraction of methanol calculated without account being taken of solute species is  $Z_{\text{MeOH}}$ .) Values of  $\bar{n}$  at 30° are only very slightly lower. An independent type of experiment allowed evaluation of the fraction of chromium(III) present as hexaquo-chromium(III) ion. This quantity evaluated in solvents as rich in methanol as  $Z_{\text{MeOH}} = 0.85$  is consistent with the  $\bar{n}$  data. Equilibrium constants for the stepwise replacement of water by methanol in  $\text{Cr}(\text{OH}_2)_{6-j}(\text{OHMe})_j^{3+}$  have been calculated from the  $\bar{n}$  data.

This paper describes experiments on the inner-sphere solvation of chromium(III) ion in the mixed solvent, water–methanol. The success of these experiments depends upon the low rate of exchange of solvent molecules between the first coordination shell of solvated chromium(III) ion and the solvent, analogous to the low rate of exchange of water molecules between the first coordination shell of hydrated chromium(III) ion and solvent water in aqueous solution.<sup>4</sup> Two types of

experiments were performed. The average number of methanol molecules bound per chromium(III) ion,  $\bar{n}$ , was evaluated after using an ion-exchange procedure to separate chromium(III) ion with its methanol-containing coordination shell from the parent solvent. An ion-exchange procedure was used also in the second type of experiment to separate hexaquo-chromium(III) ion from the mixture of aquomethanol–chromium(III) species present at equilibrium in solutions in the mixed solvents. With an isotopic dilution procedure establishing the extent of recovery of hexaquo-chromium(III) ion, the fraction of chromium(III) present as hexaquo-chromium(III) ion,  $\alpha_0$ , was accessible.

The relationships of these two functions  $\bar{n}$  and  $\alpha_0$  to the concentrations of species  $\text{Cr}(\text{OH}_2)_{6-j}(\text{OHMe})_j^{3+}$

(1) Taken from the Ph.D. thesis of Jerrold C. Jayne, University of Wisconsin, 1963. Presented at the Solvation Symposium sponsored by the Chemical Institute of Canada at Calgary, Alberta, August 29, 1963.

(2) This work was supported in part by the Research Committee of the Graduate School, University of Wisconsin, the United States Atomic Energy Commission (Contract AT(11-1)-1168 (U. of Wisconsin)), and the National Science Foundation (Grant GP-680 (U. of Colorado)).

(3) Author to whom inquiries should be addressed, Department of Chemistry, University of Colorado.

(4) J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951).