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The Kinetics of the Successive Ammonation Reactions of Tetrachloropalladate(II) Ion[1]

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On treatment with buffered micromolar concentrations of ammonia, $PdCl_4^{2-}$ is converted into an equilibrium mixture of $Pd(NH_3)_2Cl_2$, $Pd(NH_3)_3Cl^+$, and $Pd(NH_3)_4^{2+}$. Two of the consecutive reaction steps may be studied under reaction conditions, of which the faster corresponds to the change $PdCl_4^{2-} \xrightarrow{k_A'} Pd(NH_3)Cl_3^-$. The slower step most probably is *cis*-$Pd(NH_3)_2Cl_2 \xrightarrow{k_B'} Pd(NH_3)_3Cl^+$. Other reaction steps in the system are too fast to be observed. Each pseudo-first-order rate constant may be represented by $k_Y' = k_{Y2}([NH_3]/[Cl^-])([Cl^-] + r_Y)$. Rate parameters found at 25°, $\mu = 1.0$ *M* are $k_{A2} = 33\ M^{-1}$, $r_A = 0.9\ M$, $k_{B2} = 12\ M^{-1}\ sec^{-1}$, $r_B = 1.1\ M$. Activation enthalpy and entropy for the first step are estimated at 20 kcal and −18 eu, respectively. Comparison is made with results for the reverse reactions and for the analogous platinum systems.

Introduction

The kinetics of substitution of ammonia by chloride ion in the chloroammine complexes of palladium(II) has been the subject of several recent investigations.[2-5] These reactions, as is typical of square-planar substitutions,[6] show two-term rate laws and negative entropies of activation. The data are consistent with significant *cis* effects, but evidence regarding the *trans* effect is equivocal.

Unlike the reactions just mentioned, ammonation (substitution of chloride by ammonia) involves the reaction of an uncharged molecule with substrate. For this reason the kinetics of ammonation should be less sensitive to effects of ionic strength or to those of the charge on the substrate and thus should be more susceptible to a straightforward interpretation. In the present work, we report kinetic studies on the ammonation of tetrachloropalladate(II), $PdCl_4^{2-}$. These experiments, carried out at very low, buffered concentrations of ammonia, lead to the formation of an equilibrium mixture of $Pd(NH_3)_2Cl_2$, $Pd(NH_3)_3Cl^+$, and $Pd(NH_3)_4^{2+}$. Graphical analysis of the absorbance–time data showed two component steps, with no evidence of a third slower step. The absorbance, *A*, is thus given by[7]

$$A - A_\infty = \Delta A = I_A e^{-k_A't} + I_B e^{-k_B't} \qquad (1)$$

Experimental Section

Materials.—Solutions containing $PdCl_4^{2-}$ were prepared from commercially available "high-purity" $(NH_4)_2PdCl_4$, used without further purification. Other chemicals used were of reagent grade.

Equipment.—Absorbance measurements were made with a Beckmann Model DU spectrophotometer, using 10-cm silica cells. Special thermostating jackets were built for operation away from room temperature. Absorbance–time data were recorded manually.

Kinetics.—Stock solutions of $PdCl_4^{2-}$ were kept at 1 *M* in chloride ion to prevent base hydrolysis. To initiate reaction, a portion of stock solution was mixed with ammonium and chloride ions in an acetic acid–sodium acetate buffer at a total ionic strength of 1.0 (maintained with sodium perchlorate). Concentration of palladium in the reacting solution was 0.5 m*M*. Ammonium and chloride ion concentrations were varied, separately, from *ca.* 0.1 to 1.0 *M*. For virtually all runs, concentrations of acetic acid and acetate ion were, respectively, 0.0100 and 0.0180 *M*. The solutions were thus buffered in ammonia at concentrations of the order of 10^{-5} *M*.

Data at 25° were carried out at three different wavelengths, 400 nm, 470 nm, and an intermediate, ranging from 415 to 435 nm. Runs were continued, typically, for perhaps five half-times, relative to the slow step; the infinite-time absorbance was measured after 24 hr.

The intermediate wavelength was chosen to give the optimum information regarding k_B' in accordance with the following. In the vicinity of 420 nm, I_A of eq 1 becomes zero. The actual wavelength of this "quasi-isosbestic"[8] depends on the ratio $[NH_4^+]:[Cl^-]$, since it must depend on ϵ_∞ (see below, "Preliminary Analysis"). Wavelengths were chosen for the runs in this region, from which k_B' was determined, so as to be close to this point, although the condition of $I_A = 0$ was never actually achieved in the kinetic runs.

Runs at 30° were carried out at 400 nm only. At this wavelength, absorbance passes through a maximum, but the maximum occurs at such long times that measurements taken in the early stages of reaction reflect the first step only.

Results

Preliminary Analysis.—Study of the infinite-time molar extinction coefficients (ϵ_∞) from various runs shows that the ultimate products of reaction are, in all cases, the equilibrium mixture of $Pd(NH_3)_2Cl_2$, $Pd(NH_3)_3Cl^+$, and $Pd(NH_3)_4^{2+}$. Using the known extinction coefficients[5] and equilibrium data[9] for these species we are able to predict the experimental values of ϵ_∞ at several wavelengths and concentrations of ammonia and chloride. As an illustration, we report

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[1] This research has been supported by the Office of Naval Research. Portions are taken from the M.S. Thesis of W. W. Monk, Naval Postgraduate School, 1968.

[2] A. J. Poë and D. H. Vaughan, *Inorg. Chim. Acta.*, **1**, 255 (1967).

[3] R. A. Reinhardt and R. K. Sparkes, *Inorg. Chem.*, **6**, 2190 (1967).

[4] J. S. Coe, M. S. Hussein, and A. A. Malik, *Inorg. Chim. Acta*, **2**, 67 (1968).

[5] R. A. Reinhardt and J. S. Coe, *ibid.*, **3**, 438 (1969).

[6] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 375 ff.

[7] Observed (pseudo-first-order) rate constants will be represented by k' with subscripts A and B referring to the fast and slow steps, respectively. I_A and I_B are constants which are functions[5] of extinction coefficients and rate constants.

[8] So called, since the slow change in absorbance (following k_B') resembles in appearance a true isosbestic point in repeated spectral scans.

[9] R. A. Reinhardt, N. L. Brenner, and R. K. Sparkes, *Inorg. Chem.*, **6**, 254 (1967).

the following values of ϵ_∞, in cm mmol^{-1}, at 400 nm (computed values in parentheses) as a function of $R = [NH_4^+]/[Cl^-]$: $R = 0.12$, ϵ_∞ 62 (59); $R = 0.37$, ϵ_∞ 78 (77); $R = 0.62$, ϵ_∞ 62 (59); $R = 1.0$, ϵ_∞ 42 (43). Since all these measurements were made on solutions containing the acetic acid–acetate ion buffer (0.028 *M* total acetate), we consider this agreement also as evidence that, at the concentrations used, no substitution by acetate ion has taken place.

On the basis of the calculations made previously,[3,10] the rate of ammonation of *trans*-$Pd(NH_3)_2Cl_2$ is seen[11] to be too fast to be observed under the conditions of the present experiments. That is to say, it may be assumed that $Pd(NH_3)_3Cl^+$ and *trans*-$Pd(NH_3)_2Cl_2$ will be in effective equilibrium. The reversible ammonation of $Pd(NH_3)_3Cl^+$ is less rapid than this, but the associated absorbance changes are utterly negligible at 475 nm and virtually so at 400 nm. We have computed the corrections to absorbance at 400 nm necessary for this last step,[12] based on the rate constants and extinction coefficients, and have found them negligible except at the two lowest concentrations of chloride ion. In view of the uncertainties of these corrections (*e.g.*, the question of the isomers of $Pd(NH_3)_2Cl_2$) we have not used the 400-nm data from these two runs in evaluating k_A'.

At 470 nm, I_B of eq 1 is very small, so that log ΔA *vs.* t is nearly a straight line of slope k_A'. Now at this wavelength, virtually all absorbance[14] is due to $PdCl_4^{2-}$, and hence dA/dt closely represents $d[PdCl_4^{2-}]/dt$. Moreover, the rate constant obtained from analysis of the early-time slopes of the runs at 400 nm (see below under "Treatment of Data") was always k_A'. Based on the foregoing, k_A' is assigned to the first step of the reaction

$$PdCl_4^{2-} + NH_3 \longrightarrow Pd(NH_3)Cl_3^- + Cl^- \qquad (2)$$

Identification of k_B' is considered in the "Discussion" section.

Treatment of the Data.[17]—The runs at 25° were analyzed by least-squares fit to the constants of eq 1, using substantially the method outlined earlier.[3] Values of k_A' were found from the runs at 400 and 470 nm (holding k_B' fixed); those for k_B', similarly, from the runs at the intermediate wavelengths. Results are shown in Table I.

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE CONSECUTIVE AMMONATIONS OF $PdCl_4^{2-}$ AT $\mu = 1.0$[a]

$t = 25°$

$10^5[NH_3]$	$[Cl^-]$	$10^3k_A'$ 400 nm	$10^3k_A'$ 475 nm	$10^3k_B'$
2.69	1.00	1.58	1.72	0.670
1.86	0.73	1.40	1.45	0.644
1.33	0.73	0.97	0.90	0.354
0.80	0.73	0.558	0.670	0.242
0.53	0.73	0.410	0.369	0.150
0.27	0.73	0.229	0.192	0.064
0.53	0.45	0.522	0.598	0.209
0.53	0.27	0.720	0.813	0.298
0.53	0.18	*b*	1.20	0.410
0.53	0.09	*b*	2.13	0.730

$t = 30°$, 400 nm

$10^5[NH_3]$	$[Cl^-]$	$10^3k_A'$
0.12[c]	1.00	0.14
0.42	0.50	0.69
0.42	0.70	0.54
0.42	0.90	0.47,[d] 0.49[e]
0.62	0.50	1.21
0.62	0.70	0.93
0.62	0.85	0.75
0.83	0.50	1.53
0.83	0.70	1.18
0.83	0.80	1.15

[a] 0.0100 *M* HOAc, 0.0180 *M* NaOAc except as stated. All concentrations in moles per liter. [b] Not included because of interference from succeeding steps. [c] 0.0099 *M* HOAc, 0.0025 *M* NaOAc. [d] 0.0050 *M* HOAc, 0.0090 *M* NaOAc. [e] 0.0200 *M* HOAc, 0.0360 *M* NaOAc.

Studies at 30° were conducted only at 400 nm and only in the initial stages (*i.e.*, before the maximum in absorbance was reached). It may be shown readily that for any consecutive reaction scheme

$$d\bar{\epsilon}/dt = -k_A'\bar{\epsilon} + k_A'\epsilon_B - k_A'(\epsilon_B - \epsilon_C)(1 - e^{-k_B't}) \qquad (3)$$

where $\bar{\epsilon}$ is the average extinction coefficient (absorbance per unit length divided by total palladium concentration). Hence a plot of $d\bar{\epsilon}/dt$ *vs.* $\bar{\epsilon}$ (or dA/dt *vs.* A) should approach linearity with slope $-k_A'$ as $t \rightarrow 0$. Derivatives were obtained numerically and the values of k_A' derived from the resulting plots are given in the lower portion of Table I. Because of the methods used, these results are of appreciably lower precision than those found at 25°.

Relevant Equilibrium Data.—For computation of the concentrations of ammonia in the various solutions we have selected K_a values for NH_4^+ as 4.25×10^{-10} at[9] 25° and[18] 5.88×10^{-10} at 30°, both for unit ionic strength. Martell and Sillén[19] quoted the following pK_a values for acetic acid at 20°, $\mu = 1$: 4.61, 4.55, 4.59. Since the temperature coefficient of K_a is virtually zero[20] near room temperature, we shall use the median value, $K_a = 2.60 \times 10^{-5}$ at both 25 and 30°. For the buffer ratio used in all but one run ([HOAc]/

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(10) Erratum: In Table II of ref 3 the value given as k_2 for $Pd(NH_3)_2Cl$ should be 1.8×10^3 (instead of 18×10^3) M^{-1} sec^{-1}.

(11) These computations assume that *trans*-$Pd(NH_3)_2Cl_2$ predominates over the *cis* isomer in equilibrium experiments and in kinetics experiments when formed from more highly ammonated species.

(12) Solving the complex mechanism by the secular-equation method, as described in ref 13a.

(13) (a) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2d ed, Wiley, New York, N. Y., 1961, p 173 ff; (b) pp 211–212; (c) p 150 ff.

(14) Relevant extinction coefficients at 470 nm are, in cm mmol^{-1}: $PdCl_4^{2-}$, 164;[15] $Pd(NH_3)Cl_3^-$, ~40;[16] *cis*-$Pd(NH_3)_2Cl_2$, ~20;[16] *trans*-$Pd(NH_3)_2Cl_2$, ~0.5

(15) Supplementary data to A. J. Cohen and N. Davidson, *J. Amer. Chem. Soc.*, **73**, 1955 (1951); in ADI Document No. 3044.

(16) Measurements in this laboratory by LCDR M. T. Midas.

(17) For supplementary material (specific kinetic data) order Document No. NAPS-01017 from ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022, remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make check payable to: CCMIC–NAPS.

(18) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1957, pp 122, 279.

(19) A. Martell and L. G. Sillén, ed., "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, pp 283–284, 364. Specific references therein.

(20) H. S. Harned and R. W. Ehlers, *J. Amer. Chem. Soc.*, **55**, 65 (1933).

[OAc$^-$] = 0.55) we thus write $10^5[NH_3] = 2.95[NH_4^+]$ at 25° and $4.15[NH_4^+]$ at 30°.

Values reported[19] for the aquation constant of $PdCl_4^{2-}$ range from 0.004 to 0.16. A value as high as this last would have a significant effect on the interpretation of our data, for it would then be neccessary to correct the observed rate constants for the concentration of $Pd(OH_2)Cl_3^-$. We have therefore examined the spectra of 0.45 m*M* $PdCl_4^{2-}$ in 1 *M* acid at concentrations of chloride ion from 1.0 to 0.09 *M*. Absorbances measured at 425 nm in 10-cm cells, with corresponding [Cl$^-$] (*M*) in parentheses were 0.400 (1.0), 0.408 (0.82), 0.420 (0.54), and 0.575 (0.090). Equilibrium appeared to be established as soon as solutions were mixed. To test the consistency with various possible values of K_{aq}, we plotted $A(1 + [Cl^-]/K_{aq})$ *vs.* [Cl$^-$]. Using $K_{aq} = 0.16$, the last point (at 0.09 *M* Cl$^-$) lies 10% high, whereas using $K_{aq} = 0.02$, all points are within 1% of the predicted straight line. Our data cannot distinguish between various small values of K_{aq} but do indicate that it is significantly less than 0.16 and enough so that no correction for aquation need be made.

Rate Constants and Rate Parameters.—In Figure 1 are plotted observed rate constants (at [Cl$^-$] = 0.7*M*) as a function of [NH$_3$]. The proportionality to [NH$_3$] is evident, as is the lack of any sign of a positive intercept to the lines. Examination of the data of Table I also shows that, at constant [NH$_3$], the rates decrease with increasing [Cl$^-$]; more carefully, the observed rate constants are linear with 1/[Cl$^-$]. We present the results in the form of eq 4 where Y is A or B,

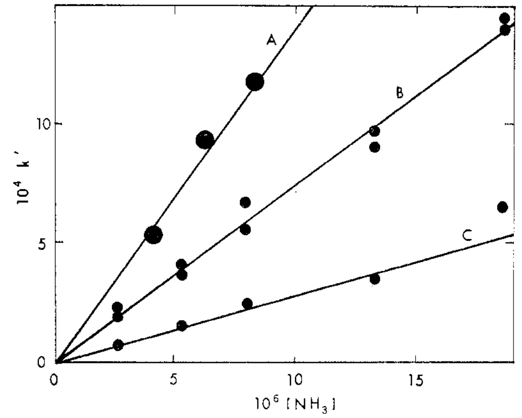

Figure 1.—Observed rate constant (sec^{-1}) *vs.* NH$_3$ concentration (*M*): A, k_A', 30°, 0.7 *M* Cl$^-$; B, k_A', 25°, 0.73 *M* Cl$^-$; C, k_B', 25°, 0.73 *M* Cl$^-$.

$$k_Y' = k_{Y2}\frac{[NH_3]}{[Cl^-]}(r_Y + [Cl^-]) \qquad (4)$$

k_{Y2} (without prime) is the corresponding second-order rate constant, and r_Y is an additional rate parameter such that $k_{Y2}r_Y$ is the rate constant with first-order dimensions corresponding to the reaction path *via* aquation. Individual rate constants thus found are: at 25°, $k_{A2} = 33\ M^{-1}\ sec^{-1}$, $r_A = 0.9\ M$, $k_{B2} = 12\ M^{-1}\ sec^{-1}$, $r_B = 1.1\ M$; and at 30°, $k_{A2} = 60\ M^{-1}\ sec^{-1}$ and $r_A = 1\ M$. Activation parameters are estimated as $\Delta H_{A2}^{\ddagger} \approx 10$ kcal and $\Delta S_{A2}^{\ddagger} \approx -20$ eu.

It is pertinent to note that the run at 30° indicated in Table I by note *c* was carried out at about 7 times the hydrogen ion concentration of all the others, yet the resulting k_A' fits eq 4 very satisfactorily, indicating that the rates are not dependent on [H$^+$], *per se*. The runs denoted by notes *d* and *e* in Table I demonstrate the independence of rate on buffer concentration by their agreement with one another and by the fit to eq 4. This latter observation reinforces our remark made earlier that acetate ion is not involved in the substitutions.

Discussion

Referring at first to k_A', it is seen that eq 4 corresponds to the usual two-term rate law for square-planar complexes. Furthermore, this relation is consistent, through the principle of microscopic reversibility,[13b] with the rate law found by Poë and Vaughan[2] for the reverse of eq 2, which may be written as

$$d[PdCl_4^{2-}]/dt = \frac{k_A}{K_2}(r + [Cl^-]) \qquad (5)$$

wherein K_2 is the equilibrium quotient for eq 2. Poë and Vaughan reported r_A as 1.5 *M* at 65°, $\mu = 1.0$, but neither their work nor ours gives a sufficiently reliable temperature coefficient for r_A to make comparison with the present result. Using the temperature coefficient reported for the second-order rate constant,[2] Coe, *et al.*,[4] have computed k_{A2}/K_2 as 2×10^{-6} at 25°. From this value we calculate $K_2 = 1.5 \times 10^7$. In similar fashion, combining the temperature coefficient data of the present work with those of Poë and Vaughan $\Delta H_2° = -23$ kcal and as $\Delta S_2° = -11$ eu.

For the general case of substitution of Y for X in L$_3$MX (square planar), the solvent-dependent (first-order) path is presumed to be

$$L_3MX + H_2O \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} L_3M(OH_2) + X \qquad (6)$$

$$L_3M(OH_2) + Y \xrightarrow{k_7} L_3MY + H_2O \qquad (7)$$

The steady-state assumption applied to the aquated intermediate leads to

$$\frac{d[L_3MY]}{dt} = \frac{k_6[Y]/[X]}{k_{-6}/k_7 + [Y]/[X]} \qquad (8)$$

Whether or not [Y]/[X] actually appears in the observed rate law will depend on the magnitude of k_{-6}/k_7 *i.e.*, on whether eq 6 or eq 7 is rate determining. For the chloroammine complexes of palladium(II), all evidence indicates that substitution of H$_2$O for Cl$^-$ or the reverse is very rapid, whereas the substitution of H$_2$O for NH$_3$ is known to be slow.[21]

The conditions of concentration used in our experiments are not greatly different from those used in the aqueous synthesis of *cis*-dichlorodiamminepalladium(II).[22] Now in order for *cis*-Pd(NH$_3$)$_2$Cl$_2$ to accumulate,

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[21] (a) L. Rasmussen and C. K. Jørgensen, *Acta Chem. Scand.*, **22**, 2315 (1968); (b) J. S. Coe and J. R. Lyons, *J. Chem. Soc. A*, 2669 (1969).

[22] (a) R. Layton, D. W. Sink, and J. R. Durig, *J. Inorg. Nucl. Chem.*, **28**, 1965 (1966); (b) A. A. Grinberg and V. M. Shul'man, *Dokl. Akad. Nauk SSSR*, 215 (1933).

its rate of decomposition must be less than its rate of formation. However, we have noted above that there is no evidence of a rate constant less than k_B'. It is thus concluded that k_B' does not represent the rate of formation of *cis*-$Pd(NH_3)_2Cl_2$; moreover, since a third reaction rate was not observed, the rate of formation of *cis*-$Pd(NH_3)_2Cl_2$ must be presumed to be significantly larger than k_A' as well. On this basis, $Pd(NH_3)Cl_3^-$ and *cis*-$Pd(NH_3)_2Cl_2$ are assumed to be in fairly rapidly established equilibrium.

There is some indication that this equilibrium lies largely in favor of *cis*-$Pd(NH_3)_2Cl_2$ in all of our experiments. The constant I_B of eq 1 is equal to[5] $[k_A'/(k_A' - k_B')](\epsilon_B - \epsilon_\infty)$, where ϵ_B is the effective extinction coefficient of the mixture of products resulting from the first step. Surprisingly, ϵ_B computed from the measured I_B values (see above, "Treatment of the Data") is virtually the same for any given wavelength, independent of the $[NH_3]/[Cl^-]$ ratio of the run. Values thus found for ϵ_B are, in cm^2 mmol^{-1}, 120 at 400 nm, 80–90 at 415 nm, and 20–30 at 470 nm. The constancy indicates that the position of equilibrium is unchanged from run to run, and the results more closely match the estimates[16] for *cis*-$Pd(NH_3)_2Cl_2$ (120, 90, and 30, respectively) than for $Pd(NH_3)Cl_3^-$ (130, 130, and 40).

The possible modes of conversion of *cis*-$Pd(NH_3)_2Cl_2$ to $Pd(NH_3)_3Cl^+$, etc., are represented by[23]

$$cis\text{-}Pd(NH_3)_2Cl_2 + NH_3 \longrightarrow Pd(NH_3)_3Cl^+ + Cl^- \qquad (9)$$

or

$$cis\text{-}Pd(NH_3)_2Cl_2 + Cl^- \rightleftharpoons Pd(NH_3)Cl_3^- + NH_3 \qquad (10a)$$

$$Pd(NH_3)Cl_3^- + NH_3 \longrightarrow trans\text{-}Pd(NH_3)_2Cl_2 + Cl^- \qquad (10b)$$

$$trans\text{-}Pd(NH_3)_2Cl_2 + NH_3 \rightleftharpoons Pd(NH_3)_3Cl^+ + Cl^- \qquad (10c)$$

On the assumption that the equilibrium of eq 10a lies well to the left, as discussed above, any contribution to k_B' by path 10 would involve an ammonia-independent term, whereas, as is seen in Figure 1, k_B' *vs.* $[NH_3]$ does not show an intercept. Though the evidence is far from conclusive, we tentatively assign k_B', based on the foregoing arguments, to the step represented by eq 9.

In Table II, following, are summarized pertinent kinetic and equilibrium data for ammonation of the chloroammine complexes of palladium(II).

In Table II for each case, k_f, which is k_{Y2} of eq 4, refers to the second-order rate constant for the indicated forward process; k_r represents the rate constant for the chloride-dependent term in the reverse process; and K the equilibrium quotient for reaction in the direction shown. For those steps involving the formation or reaction of *trans*-$Pd(NH_3)_2Cl_2$ (note *f*) K and k_f are reported on the assumption that the *trans* isomer predominates over the *cis* at equilibrium. If in fact the equilibrium mixture contains appreciable *cis*-$Pd(NH_3)_2Cl_2$, the entries will be correspondingly smaller for $Pd(NH_3)Cl_3^- \rightarrow$ *trans*-$Pd(NH_3)_2Cl_2$ and larger for *trans*-$Pd(NH_3)_2Cl_2 \rightarrow Pd(NH_3)_3Cl^+$.

TABLE II

EQUILIBRIUM CONSTANTS AND FORWARD AND REVERSE SECOND-ORDER RATE CONSTANTS FOR AMMONATION AT 25°, $\mu = 1.0\ M$

Process	$10^{-5}K$[a]	k_f, M^{-1} sec^{-1}	k_r, M^{-1} sec^{-1}
$PdCl_4^{2-} \rightarrow Pd(NH_3)Cl_3^-$	200[b]	33[c]	0.02[d]
$Pd(NH_3)Cl_3^- \rightarrow$ *cis*-$Pd(NH_3)_2Cl_2$	. . .	. . .	14[d]
$Pd(NH_3)Cl_3^- \rightarrow$ *trans*-$Pd(NH_3)_2Cl_2$	5[e]	4[e,f]	0.069[d]
cis-$Pd(NH_3)_2Cl_2 \rightarrow Pd(NH_3)_3Cl^+$	. . .	(12)[g]	. . .
trans-$Pd(NH_3)_2Cl_2 \rightarrow Pd(NH_3)_3Cl^+$	0.62[e]	1800[e,f]	300[h]
$Pd(NH_3)_3Cl^+ \rightarrow Pd(NH_3)_4^{2+}$	0.16	120[f]	71[h]

[a] Equilibrium data from ref 9 except as noted. [b] Computed from rate constants. [c] Present work. [d] Reference 2. [e] Assumes *trans*-$Pd(NH_3)_2Cl_2$ predominates over *cis*-$Pd(NH_3)_2Cl_2$ at equilibrium. See text. [f] Computed from K and k_r. [g] Present work, assuming k_B' to represent this step. [h] Reference 3.

Comparison of k_f from Table II with the results of Martin, *et al.*,[24] for the corresponding platinum complexes shows a striking similarity in pattern, and thus indicates qualitatively the operation of *trans* and *cis* effects. Quantitatively, the k_f data may be represented by use of an equation of exactly the form given[24] for the platinum series

$$k_f/n = x(y)^m(z)^p \qquad (11)$$

where n is the number of equivalent chlorides, m the number of NH_3 ligands *trans* to the leaving chloride, and p the number of NH_3 *cis* to the leaving chloride. Setting $x = 8$, $y = 0.1$, and $z = 10$, all the k_f data of Table II are fit to within 20% except for the process $Pd(NH_3)Cl_3^- \rightarrow$ *trans*-$Pd(NH_3)_2Cl_2$. For the latter, eq 11 with these parameters predicts $k_f = 0.8$.

The data for the corresponding platinum complexes require[24] $x = 1.0 \times 10^{-4}$, $y = 0.2$, and $z = 5$. The one process which is not properly so represented is, no doubt coincidentally, that for the formation of *trans*-$Pt(NH_3)_2Cl_2$. The larger *trans* and *cis* effects for Pd relative to Pt are consistent with results found by Pearson and Johnson[25] in substitutions in acetylacetonato complexes of Pd(II). The increased overall rate for the palladium complexes, by about 10^5, is similar to that found for the reverse reactions[3] and follows the trend observed by Basolo, Gray, and Pearson.[26]

The analysis of *cis* and *trans* effects is less satisfactory for the reverse reactions. The increased reactivity toward chloride ion of $Pd(NH_3)_3Cl^+$ over $Pd(NH_3)_4^{2+}$ has been observed by Reinhardt and Sparkes[3] and also by Coe, Hussein, and Malik[4] as reinterpreted.[5] It is difficult not to attribute this difference to the enhanced *trans* effect of Cl^- relative to NH_3. Likewise the decreased rate of reaction of *cis*-$Pd(NH_3)_2Cl_2$ compared with $Pd(NH_3)_3Cl^+$ shows the *cis* deactivation by Cl^-. The very low rate of reaction of *trans*-$Pd(NH_3)_2Cl_2$ with Cl^-, in which the leaving group is *trans* to NH_3 and *cis* to two chlorides is also consistent with the pattern, but the rate of the reaction $Pd(NH_3)Cl_3^- \rightarrow PdCl_4^{2-}$ is unexpectedly slow: based on the effects

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[23] The symbol $\rightleftharpoons$ is used for a rapid, reversible process.

[24] C. B. Colvin, R. C. Gunther, L. D. Hunter, J. A. McLean, M. A. Tucker, and D. S. Martin, Jr., *Inorg. Chim. Acta*, **2**, 487 (1968).

[25] R. G. Pearson and D. A. Johnson, *J. Amer. Chem. Soc.*, **86**, 3983 (1964).

[26] F. Basolo, H. B. Gray, and R. G. Pearson, *ibid.*, **82**, 4200 (1960).

shown with the rest of the system, k_r for this step would be anticipated as about 0.5.

Coe, *et al.*,[4] have pointed out that ionic strength effects could mask the true *trans* and *cis* effects. A reasonable assumption is that infinite dilution would be the more appropriate medium for comparison. While actual extrapolation cannot be made from such concentrated solutions, qualitative prediction is possible from the fact that many 1:1 electrolytes show a minimum in activity coefficient[27] in the range of 0.3–0.5 *M*. Based on this and on the usual kinetic assumptions,[13c] it can be said that k_r for the formation of $PdCl_4^{2-}$ would be even less at $\mu = 0$ than at $\mu = 1$ and[28] hence the deviation from expected behavior will be even more pronounced than seen from Table II.

It is not unreasonable to seek the source of the anomaly in the thermodynamics of the system. As is shown elsewhere,[9] the last three values of *K* from Table II, when corrected statistically, differ by small factors (1.5–3) and in a direction consistent with the decreased ease of losing Cl^- as the substrate charge becomes more positive. The equilibrium constant for $PdCl_4^{2-} \rightleftarrows Pd(NH_3)Cl_3^-$ is, however, an order of magnitude too large for the trend shown by the other three constants. It then appears that k_r reflects the thermodynamics of the reactions more closely than does k_f or that the transition state more closely resembles the chloride-rich species of the reaction step. This last conclusion is consistent with the idea that it should require more energy to dissociate ammonia than chloride from the presumed[6] five-bonded intermediate.

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[27] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

[28] In accord with the foregoing is the fact that Poë and Vaughan[2] found a smaller rate at $\mu = 5$ than at $\mu = 1$.

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Phosphorus-31 Nuclear Magnetic Resonance Study of Trivalent Phosphorus Derivatives of Metal Carbonyls[1]

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The ^{31}P nuclear magnetic resonance spectra of a large group of metal carbonyl derivatives have been obtained. The study of about 60 derivatives, $M(CO)_{m-n}(PA_3)_n$ ($M = Ni$, $m = 4$; $M = Cr$, Mo, W, $m = 6$; $1 < n < 4$; and $A = F$, Cl, OCH_3, SCH_3, $N(CH_3)_2$, CH_3, C_2H_5), has allowed us to define a typical behavior of ^{31}P chemical shift when *n* varies. A qualitative rationalization of the characteristic shifts in terms of $\sigma + \pi$ charge transfer is proposed.

Nuclear magnetic resonance studies of phosphorus-containing metal carbonyl derivatives have developed considerably during the last few years. Nevertheless attempts to interpret the chemical shift of the ^{31}P nucleus have met with difficulties because of the large number of factors which must be taken into consideration.[3]

The first attempt at rationalizing ^{31}P chemical shift is found in a publication by Meriwether and Leto.[4] These authors, limiting their studies essentially to the derivatives of nickel tetracarbonyl, tried to assess the relative importance of the factors influencing the chemical shift of the ^{31}P nucleus. One of their conclusions was that $\delta(^{31}P)$ appears to be dependent upon phosphorus–metal σ bond, the contribution of metal–phosphorus d_π–d_π bond being weak or constant.

Grim, *et al.*, undertook a similar study of group VI metal carbonyl derivatives whose degree of substitution was at the most two.[5,6] These authors postulated the possibility of a major contribution from d_π–d_π back-donation.

In order to develop these initial studies further, we undertook the systematic examination of a larger number of nickel tetracarbonyl derivatives and of group VI metal carbonyls whose degree of substitution *n* varies from 1 to 4.

Experimental Section

The phosphorus-31 nmr measurements were performed on a Varian Associates DP 60 spectrometer at 24.3 MHz. In most cases the compounds were examined in benzene solution.

The chemical shifts (in ppm *vs.* 85% H_3PO_4) are accurate to ±1 ppm.

The infrared spectra of the compounds in the carbonyl region were measured in hexadecane solution with a Perkin-Elmer Model 225 spectrometer, calibrated by saturated water vapor lines.

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[3] J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, **2**, 345 (1969), and references therein.

[4] L. S. Meriwether and J. R. Leto, *J. Amer. Chem. Soc.*, **83**, 3192 (1961).

[5] S. O. Grim, D. A. Wheatland, and W. McFarlane, *ibid.*, **89**, 5573 (1967).

[6] S. O. Grim and D. A. Wheatland, *Inorg. Chem.*, **8**, 1716 (1969).