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intramolecular first-order rate determining step. It is believed that this difference is due to the lower redox potential of the amine complexes of trivalent nickel as compared with that of the corresponding copper complexes.[4,7][15,16] However, it is found also for the trivalent nickel that complexes with amino acids as ligands are less stable than complexes with ethylenediamine.

One might be tempted to suggest that tetravalent nickel complexes are formed as intermediates in the second-order disappearance reactions of the trivalent complexes. Tetravalent nickel complexes with oxides and fluorides are known. The formation of a tetravalent nickel complex with ethylenediamine has been suggested as one explanation for some observations in the corresponding electrochemical system.[7] However, no kinetic or spectroscopic evidence for the formation of such an intermediate was found in this study.

(15) I. Fried and D. Meyerstein, *J. Electroanal. Chem. Interfacial Electrochem.*, **29**, 491 (1971).

(16) D. C. Olson and J. Vasilenkis, *Inorg. Chem.*, **10**, 463 (1971).

# Aquation Kinetics of the Aquoammine Complexes of Palladium(II)[1]

BY WILLIAM J. DeBERRY, JR., AND RICHARD A. REINHARDT*

Upon treatment with excess aqueous $HClO_4$, $Pd(NH_3)_4{}^{2+}$ is converted through four consecutive steps to $Pd(OH_2)_4{}^{2+}$. Correlation of observed rate constants with actual mechanistic steps is based primarily on reconstruction of the absorption spectra of the intermediate species; it was thus found that the rate constants decrease steadily from one step to the next. At 50°, $\mu = 1$, rate constants found are respectively 0.020, 0.008, $9.2 \times 10^{-3}$, and $2.2 \times 10^{-4}$ sec$^{-1}$. Activation enthalpies range from 21 to 24 kcal/mol and activation entropies from +4 to −4 eu. Substituent effects are compared with those in chloride-containing complexes and with those for the reverse reactions.

## Introduction

As a logical continuation of previous kinetic studies[2-6] in the chloroammine complexes of palladium(II), we have investigated the rates of substitution of ammonia by water in the aquoammine series. Acidification of $Pd(NH_3)_4{}^{2+}$, in the absence of complexing anions, results in stepwise aquation

$$Pd(NH_3)_4{}^{2+} + nH^+ + nH_2O = nNH_4{}^+ + Pd(NH_3)_{4-n}(OH_2)_n{}^{2+}$$

$$(1)$$
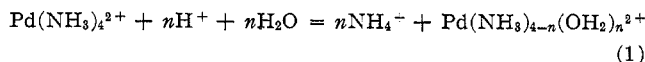
The rate of the first step of this equation is obtained from the chloride-independent term in the rate law for chloride substitution.[3-5] Rasmussen and Jørgensen,[7] incidental to their equilibrium studies in the palladium ammine–hydrogen ion system, have given approximate values at 20 and 25° for the first rate constants of the two steps of eq 1. Coe and Lyons[8] have shown clearly that the second step leads to the formation of a preponderance of the cis isomer of $Pd(NH_3)_2(OH_3)_2{}^{2+}$.

Although it has been asserted that only two steps of eq 1 take place,[3,8] graphical analysis[9] of our preliminary data at room temperature showed three components—*i.e.*, three steps—in an 8-hr run. Moreover, when the systems were allowed to stand for several days or when runs were conducted at elevated temperatures, the final systems yielded a spectrum very similar to that reported[7] for $Pd(OH_2)_4{}^{2+}$: maximum absorbance at 380 nm with a molar absorptivity of about 80 cm$^2$ mmol$^{-1}$. We thus conclude that eq 1 proceeds through four consecutive steps, ultimately to form tetraaquopalladium(II) ion.

## Experimental Section

**Materials.**—Solutions of $Pd(NH_3)_4(ClO_4)_2$ were prepared[3] by the addition of the stoichiometric quantity of silver perchlorate to a solution of $Pd(NH_3)_4Cl_2$, prepared from *trans*-$Pd(NH_3)_2Cl_2$ as described previously.[10]

**Equipment.**—Absorbance measurements were made with either a Beckman Model DU (manual operation) or a Model DK-1A (recording) spectrophotometer, using silica cells with thermostated cell holders which controlled actual cell temperature.

**Kinetics.**—All runs were carried out in 1.0 *M* perchloric acid (ionic strength 1.0). Runs were initiated by injecting the palladium solution into the acid, appropriate concentrations being used to allow for the volumes of reagents. Absorbance–time readings were continued until virtually all change had ceased. For the majority of runs a stable infinite-time absorbance ($A_\infty$) could be obtained.

Each run was carried out at a fixed wavelength in the range 300–420 nm. The use of several wavelengths at each temperature assisted in the assignment of rate constants to the mechanistic steps as is discussed below.

A few runs at 25° were carried out in 10-cm absorbance cells at 0.443 m*M* Pd(II); all the remainder made use of 5.33 m*M* Pd(II) in 1-cm cells.

## Results

**Treatment of the Data.**[11]—In a number of runs the

(1) This research has been supported by the Office of Naval Research. Based on the M.S. Thesis of W. J. DeBerry, Jr., Naval Postgraduate School, 1971.

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

(3) J. S. Coe, M. S. Hussein, and A. A. Malik, *ibid.*, **2**, 67 (1968).

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

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

(6) R. A. Reinhardt and W. W. Monk, *ibid.*, **9**, 2026 (1970).

(7) L. Rasmussen and C. K. Jørgensen, *Acta Chem. Scand.*, **22**, 2315 (1968).

(8) J. S. Coe and J. R. Lyons, *Inorg. Chem.*, **9**, 1775 (1970).

(9) K. R. Ashley and R. E. Hamm, *ibid.*, **5**, 1645 (1966).

(10) R. A. Reinhardt, N. L. Brenner, and R. K. Sparkes, *ibid.*, **6**, 254 (1967).

(11) For supplementary material (specific kinetic data) order document NAPS-01810 from ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022; remitting $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make check payable to: CCMIC-NAPS.
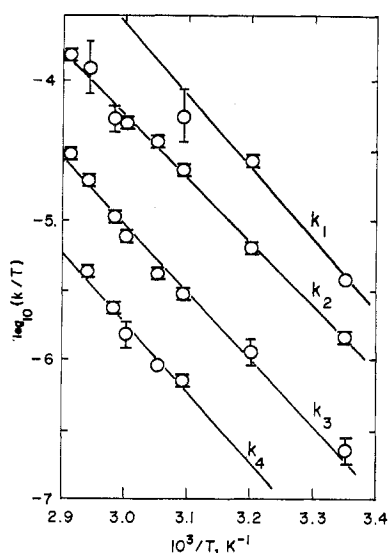
Figure 1.—Temperature dependence of rate constants (sec$^{-1}$). Where an error bar is not shown, precision is estimated as $\pm2\%$.

measured $A_\infty$ values were used; in others, the Guggenheim method[12] of analysis was employed, the fixed-time increment, $\Delta$, being selected to be of the order of the half-time for the slowest observable step. Plots of $\log \Delta A$ ($\Delta A = A_t - A_\infty$ or $A_t - A_{t+\Delta}$, as appropriate) became linear at long times and could be resolved into a series of first-order components, much as described by Ashley and Hamm.[9] That the results were not dependent on the total palladium concentration is also indicative of the first-order character of all steps.

A refined graphical analysis was then conducted as follows. The absorbance–time relation is given as $\Delta A = \Sigma I_i e^{-k_i t}$, one term for each step observed.[4] Once approximate $I$ and $k$ values have been obtained, improvement may be accomplished by the use of eq 2 for each step $j$, starting with the slowest

$$\ln [\Delta A - \sum I_i e^{-k_i t}] = -k_j t + \ln I_j \quad (i \neq j) \quad (2)$$

The resulting straight-line plots[13] of the left side of eq 2 *vs. t* gave quickly converging values of the rate constants and intercepts.

Although there was no run for which reliable values of all four rate constants could be obtained, the plot of $\log k/T$ *vs. 1/T*, even with preliminary results, showed the points falling on four lines, corresponding to the four consecutive steps. Figure 1 shows thus representative values of the final data (refined as discussed immediately below).

At lower temperatures, the slowest step is so slow that it was impractical to carry out runs for the long times involved. Runs at these temperatures were analyzed using the Guggenheim method, with $\Delta$ appropriate for the next slowest step. In order to obtain coherent results, it was found necessary to estimate $I$ and $k$ for the slowest step and include them in the left-hand side of eq 2. Estimate of $k_{slowest}$ was made from the temperature dependence observed at higher tem-

peratures (Figure 1). Intercepts appropriate to the Guggenheim plots are given by $I_{Gugg} = I_\infty(1 - e^{-k\Delta})$, where $I_\infty$ is the intercept that would be obtained if the data $[(A - A_\infty), t]$ were employed. The required $I_\infty$ for the slowest step is computed by methods to be described in the next section.

Similarly, at some of the higher temperatures, the first step and sometimes even the second is so fast that its effect disappears after a time too short for valid observation. For even when the data might afford a crude evaluation of the parameters of the fastest step, the cumulative errors involved in analyzing the fastest step, combined with uncertainties in mixing at early times, render such evaluation dubious. In a few such cases, it was found desirable to include in the analysis *via* eq 2 an extrapolated $k$ and a computed $I$ for the fast step.

Table I lists the resulting rate constants at various

TABLE I

RATE CONSTANTS[f] AND ACTIVATION PARAMETERS FOR THE CONSECUTIVE STEPS IN THE SUBSTITUTION OF NH$_3$ BY H$_2$O IN Pd(NH$_3$)$_4{}^{2+}$

| Temp, °C | λ, nm | $10^3 k_1$ | $10^3 k_2$ | $10^3 k_3$ | $10^3 k_4$ |
|---|---|---|---|---|---|
| 25 | 300[g] | 1.16[a] | 0.57[b] | 0.09[d] | |
| | 300 | 1.05[a] | 0.49[b] | 0.11[d] | |
| | 305[g] | 1.15[a] | 0.44[b] | 0.071[c] | |
| | 310[g,h] | 1.10[a] | 0.40[b] | 0.067[c] | |
| 39 | 310 | 8.5[b] | 2.09[b] | 0.37[c] | |
| | 396 | 8.4[b] | 2.27[b] | 0.46[c] | i |
| | 400 | | 1.74[b] | 0.342[b] | i |
| 40 | 310 | 8.2[c] | 1.91[a] | 0.312[a] | |
| | 396 | | 2.38[b] | 0.475[a] | i |
| 50 | 310 | 18[d] | 7.6[b] | 0.93[b] | 0.229[a] |
| | 320 | | 9[e] | 0.96[b] | 0.236[a] |
| | 328 | | 11[d] | 0.92[b] | 0.165[b] |
| | 396 | | 6.9[c] | 1.33[a] | i |
| 55 | 323 | | | 1.43[b] | 0.314[a] |
| | 340 | | 12.7[b] | 1.35[b] | 0.300[a] |
| | 350 | | 11[c] | 1.36[b] | 0.286[a] |
| 60 | 360 | | 17[c] | 2.23[b] | 0.512[b] |
| | 380 | | 16.6[b] | 2.52[b] | 0.39[c] |
| | 400 | | 15.9[b] | 2.59[a] | i |
| | 420 | | 13[d] | 3.6[c] | 0.68[c] |
| 63 | 325[h] | | 20[e] | 3.56[b] | 0.77[b] |
| | 350[h] | | 18[c] | 3.74[b] | 0.771[a] |
| 67 | 310 | | 42[d] | 6.8[b] | 1.73[b] |
| | 325 | | i | 6.2[b] | 1.48[a] |
| 70 | 396 | i | 53.1[b] | 11.0[b] | i |
| $\Delta H^{\ddagger}$, kcal mol$^{-1}$ | | $23 \pm 1$ | $21 \pm 1$ | $22 \pm 1$ | $24 \pm 2$ |
| $\Delta S^{\ddagger}$, cal mol$^{-1}$ K$^{-1}$ | | $+4 \pm 4$ | $-4 \pm 2$ | $-4 \pm 4$ | $0 \pm 6$ |

[a] $\pm2\%$. [b] $\pm10\%$. [c] $\pm20\%$. [d] $\pm40\%$. [e] Estimate only. [f] 5.33 m$M$ in Pd except as noted. All at $\mu = 1.0$. [g] 0.443 m$M$ in Pd. [h] Average of two runs. [i] Isosbestic.

temperatures and wavelengths. (The assignment of rate constants to the mechanistic steps is discussed in the next section.) Errors given for individual rate constants represent the estimated uncertainties, as developed during the successive applications of eq 2.

In this table are also included activation parameters, obtained by a least-squares fit from Figure 1, points being weighted inversely proportionately to the errors estimated from the scatter of the data at each temperature. Errors given in the table for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are somewhat larger than those found by deviations from the computed line, so as to allow for variations in weighting procedure.

(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 49.
(13) The calculations were carried out on a Wang 700A programmable computer, made available through the kindness of Professor J. E. Sinclair of this department.

**Assignment of Rate Constants.**—It has been pointed out elsewhere[4] that in a complex reaction wherein a "spectrum" of rate constants is observed by absorption methods, it is by no means obvious which experimental rate constant is to be associated with which step of the mechanism. It has been assumed, in the presentation of Table I, that which will now be demonstrated: that the first step is the fastest and that the rate constants decrease from step to step. For the successive aquations of tetraamminepalladium(II) ion the mechanism assumed is

$$Pd(NH_3)_{5-i}(OH_2)_{i-1}{}^{2+} + H_2O \longrightarrow Pd(NH_3)_{4-i}(OH_2)_i{}^{2+} + NH_3 \tag{3}$$
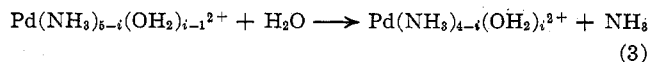
for $i = 1$–4. We shall denote the rate constant corresponding to a given step as $k_i$.

Rasmussen and Jørgensen[7] carried out preliminary studies on the early stages of reaction by observing pH *vs. t*, and their results show zero-order dependence on the concentration of $H^+$. (Although those experiments involved only $k_1$ and $k_2$, there is no reason to expect any acid dependence of $k_3$ or $k_4$ either, since none has been found in any of the various systems studied[2,3,5] wherein $NH_3$ is replaced by $H_2O$.) Since $-d[H^+]/dt$ is readily related to the rate of ligand substitution, it is easily demonstrated, from the data provided in their paper (Figure 2 in ref 7), that $k_1 > k_2$ (their $k_{-4}$ and $k_{-3}$, respectively) and not the reverse. The $k_1$ found by them at 25° is $7.8 \times 10^{-4}$ sec$^{-1}$; this value is low, as is to be expected if obtained from the slope of the $[H^+]$ *vs. t* line, since this slope is distorted by the occurrence of the second step.

Further confirmation of our identification of $k_1$ with the fastest step comes from the agreement of our value at 25° (0.0011 sec$^{-1}$) with the previously obtained 0.0011 ($\mu = 1$)[5] and 0.00109 ($\mu = 0.25$).[3,4]

The remainder of our assignment is based strongly on the observed intercepts[11] of eq 2. Integration of the rate law of the four-step mechanism (3) leads to

$$\Delta A = \sum_{i=1}^{4} I_i e^{-k_i t} \tag{4}$$

The intercepts are defined by

$$I_i = \sum_{j=i}^{4} Q_{ij} \Delta E_j \tag{5}$$

in which $Q_{11} = 1$ and, for $j \neq 1$

$$Q_{ij} = (-1)^j \frac{k_i}{k_j} \prod_{m \neq i}^{j} \frac{k_m}{k_m - k_i} \tag{6}$$

In eq 5, $\Delta E_j$ represents the change in absorbance (per unit cell length) from infinite time that is due to the species $Pd(NH_3)_{5-j}(OH_2)_{j-1}{}^{2+}$. That is, representing molar absorptivities by $\epsilon$ and using $C$ and $d$ for total palladium concentration and path length, respectively, $\Delta E_j = (\epsilon_j - \epsilon_5)C/d$.

First of all, it was noted in scans showing spectra at various time intervals that an isosbestic point develops at around 396 nm during the latter stages of the runs. That this isosbestic point corresponds to the slowest step is shown from the fact that the slowest rate is the one missing from the runs at such wavelengths (see Table I). Furthermore, the spectra for $Pd(NH_3)(OH_2)_3{}^{2+}$ and $Pd(OH_2)_4{}^{2+}$ cross at about 395 nm—*i.e.*, $\Delta E_4 = 0$. Equation 5 shows that $I_4$ is propor-

tional to $\Delta E_4$. It is thus unavoidable to conclude that the fourth step is the slowest.

For other wavelengths, application of eq 5 and 6, combining the known[7] absorptivity of $Pd(OH_2)_4{}^{2+}$ with our measured intercept for the slowest step[11] and the various rate constants (assuming step 4 is the slowest), permits computation of the absorptivity of $Pd(NH_3)(OH_2)_3{}^{2+}$. The resulting agreement with the previously reconstructed spectrum[7] for this species is shown in Figure 2, where the closed circles show our
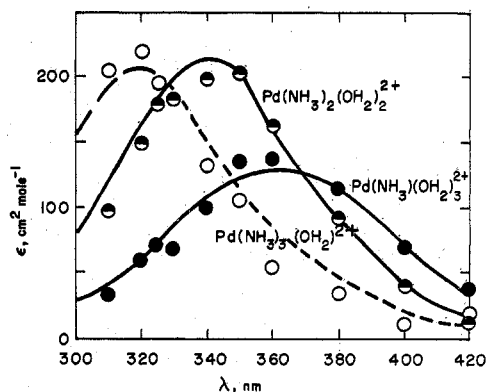


Figure 2.—Absorption spectra for some Pd(II) complexes: circles, computed from eq 5 and 6; solid curves, from ref 7; dashed curve, interpolated from data in ref 7.

computation and the solid line shows the data of Rasmussen and Jørgensen.

Similar calculations were made for the absorptivities of $Pd(NH_3)_2(OH_2)_2{}^{2+}$ and $Pd(NH_3)_3(OH_2){}^{2+}$. Assuming step 2 is the second fastest and step 3 the third fastest leads to the results also shown in Figure 2 (half circles and open circles, respectively). The broken line shown for $Pd(NH_3)(OH_2)_3{}^{2+}$ has been obtained by interpolation between the spectra[7] for $Pd(NH_3)_4{}^{2+}$ and $Pd(NH_3)_2(OH_2)_2{}^{2+}$, assuming a linear shift in wave number. Reversing the assignments of $k_2$ and $k_3$ leads to quite unacceptable spectra for the two species, the computed absorptivities being appreciably negative in many cases.

As further confirmation of this assignment, analog-computer simulations[14] of spectral scans of a run at 25° were carried out for a variety of permutations of the rate constants. Consistency with observation was possible only with the assignment given, namely, that each step in the mechanism is slower than the preceding.

## Discussion

The activation parameters from Table I are not known with sufficient precision to establish whether the trend in rate constant is the result of entropy or of enthalpy effects. The decrease in entropy upon activation is unusually small for an associative process,[15] as was also observed in the substitution[3] of $NH_3$ by $Cl^-$. Now for the latter reaction, $\Delta S^\circ$ ranges from[6,10] $+11$ to $+13$ eu and should not be greatly different for the substitution of $NH_3$ by $H_2O$, inasmuch as the partial molal entropies of chloride ion and water are

(14) Using equipment of the Computer Laboratory of the Electrical Engineering Department of this school.

(15) L. Cattalini, *Progr. Inorg. Chem.*, **13**, 285 (1970).

of comparable magnitude.[16] Thus the entropy of the activated complex lies below the average of those for the terminal states.

The positive $\Delta S^{\ddagger}$ found for the first step is in fair agreement with that (10 eu) found by Coe, *et al.*[3] If, in fact their points were included in Figure 1, they would be seen to lie close to our line, though about 20% low at 15 and 25°. On the other hand, the previous results from this laboratory[5] regarding $k_1$ are in considerable disagreement at temperatures above 25°.

In Table II are summarized rate constants at 25°,

TABLE II

FORWARD AND REVERSE RATE CONSTANTS AT 25°, $\mu = 1$, FOR REPLACEMENT OF $NH_3$ BY $H_2O$ IN Pd(II) COMPLEXES

| Complex | Cis ligands | $10^4 k_f/n$, sec$^{-1}$ | $10^{-3} k_r/n$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| **Trans NH_3** | | | |
| 1. $Pd(NH_3)_4{}^{2+}$ | $NH_3, NH_3$ | 2.75 | 7.0,[e] 18[g] |
| 2. $Pd(NH_3)_3(OH_2)^{2+} \rightarrow$ cis[b] | $NH_3, OH_2$ | 2.1 | 6.7[e,i] |
| 3. $Pd(NH_3)_3Cl^+ \rightarrow$ cis | $NH_3, Cl^-$ | | $\sim$5[f,g] |
| 4. trans-$Pd(NH_3)_2Cl_2$ | $Cl^-, Cl^-$ | 0.018[c] | $\sim$0.5[c,g] |
| **Trans OH_2** | | | |
| 5. cis[b]-$Pd(NH_3)_2(OH_2)_2{}^{2+}$ | $NH_3, OH_2$ | 0.26[h] | 21[e,i] |
| 6. $Pd(NH_3)(OH_2)_3{}^{2+}$ | $OH_2, OH_2$ | 0.13[h] | 13[e] |
| **Trans Cl^-** | | | |
| 7. $Pd(NH_3)_3Cl^+ \rightarrow$ trans[a] | $NH_3, NH_3$ | 9.0[a] | 6[a,g] |
| 8. cis-$Pd(NH_3)_2Cl_2$ | $NH_3, Cl^-$ | 2.4[c] | |
| 9. $Pd(NH_3)Cl_3{}^-$ | $Cl^-, Cl^-$ | 0.02[d] | 1.5[f,g] |

[a] Reference 5. [b] Reference 7, 8. [c] Reference 2. [d] Estimated from the data of ref 2. [e] Using equilibrium data from ref 7. [f] Reference 6. [g] Equilibrium quotients for substitution of $Cl^-$ by $H_2O$ estimated: cis-$Pd(NH_3)_2Cl_2$, 0.005; $Pd(NH_3)Cl_3{}^- \rightarrow$ trans, 0.01; $PdCl_4{}^{2-}$, 0.02 from footnote *j*. Other equilibrium data from ref 6 and 10. [h] Extrapolated from 50° so as to maintain the ratio of rate constants. [i] Assuming cis-$Pd(NH_3)_2(OH_2)_2{}^{2+}$ to predominate over *trans* at equilibrium. [j] S. A. Shchukarev, O. A. Lobaneva, and M. A. Kononova, *Vestn. Leningrad. Univ., Fiz., Khim.*, **10**, 152 (1961); L. G. Sillén, Ed., *Chem. Soc., Spec. Publ.*, **No. 17**, 284 (1964).

unit ionic strength, for the known cases involving the interchange of ligand ammonia with water in the chloroaquoammine complexes of palladium(II). The table is arranged according to the ligand trans to the leaving group. Data are presented as $k/n$ where $n$ is the number of equivalent leaving groups. The symbol $k_f$ refers to the substitution of $NH_3$ by $H_2O$. For the reverse process $k_r$ is used; this has been computed from $k_f$ and, where possible, the measured equilibrium quotient. For several cases it has been necessary to combine the equilibrium quotient for substitution of $NH_3$ by $Cl^-$ with that estimated for substitution of $Cl^-$ by $H_2O$ in the chloro product.

Looking first of all at the results from the present

(16) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed, Prentice-Hall, New York, N. Y., 1952, pp 39, 54. Statistical corrections to these entropies are in general less than experimental errors and have therefore not been included.

study, the marked drop from $k_2$ to $k_3$ (lines 2 and 5 in Table II) is most reasonably explained as due to the enhanced trans effect of $NH_3$ relative to $OH_2$. This order in trans effect, it may be noted, is consistent with the qualitative order observed in the preparative chemistry of platinum(II).[15] A small cis activation of $NH_3$ compared to that of $OH_2$ appears from the comparisons between $k_1$ and $k_2$ and between $k_3$ and $k_4$ (lines 1, 2, 5, and 6) but statistical effects are actually predominant.

Regarding $k_f$ in complexes containing chloride, it will be seen that cis deactivation due to $Cl^-$ is very marked (lines 2, 4, 7, 8, and 9). The trans effect of chloride is, however, inconsistent, being significant for the highly ammonated species (lines 1 and 7) but nonexistent at the chloro end of the series (lines 4 and 9). Interestingly, the effect on rates of changing nucleophile from $H_2O$ to $Cl^-$ varies in the same general way as does the trans effect. Values for $k_{Cl^-}/k_{H_2O}$ (in l. mol$^{-1}$) are as follows: $Pd(NH_3)_4{}^{2+}$,[5] 6.5; $Pd(NH_3)_3Cl^+$,[5] 32; cis-$Pd(NH_3)_2Cl_2$,[2] 3.0; trans-$Pd(NH_3)_2Cl_2$,[2] 1.9; $Pd(NH_3)Cl_3{}^-$,[6] 1.1.

For the substitution of $OH_2$ by $NH_3$ (last column of Table II) in the complexes containing no $Cl^-$ virtually all the variation in rate constant is statistical. No appreciable distinction between $NH_3$ and $OH_2$ appears in either cis or trans position (the apparent slight trans activation of $NH_3$ is surely spurious). Thus the trend in the equilibrium quotients[7] mirrors closely that in the forward rate constants. For the complexes which do contain chloride, there appears to be a real cis deactivation due to $Cl^-$ (lines 1, 3, 4, 7, 9) and perhaps no trans effect due to $Cl^-$; uncertainties in the equilibrium data, however, render these conclusions tentative, at best. In contrast, for the substitution of $Cl^-$ by $NH_3$, as previously reported,[6] the rates change by an order of magnitude due to the trans activation or cis deactivation of chloride ion relative to ammonia.

Assuming thus no substituent effect ($OH_2$ *vs.* $NH_3$) on the rates of ammonation of the aquoammine complexes and making use of the above-noted cis and trans effects for the forward reactions, we estimate that the rate for $Pd(NH_3)_3(OH_2)^{2+} \rightarrow$ trans-$Pd(NH_3)_2(OH_2)_2{}^{2+}$ will be $(2-3) \times 10^{-5}$ sec$^{-1}$ (about one-seventh the rate of formation of the cis isomer), whereas the reverse rate constant should be about the same as for the cis: *ca.* $10^4$ sec$^{-1}$ l. mol$^{-1}$. It then follows that the cis isomer will comprise about 85% of the $Pd(NH_3)_2(OH_2)_2{}^{2+}$ present, in either equilibrium experiments or aquation kinetics experiments. This prediction is in agreement with previous assumptions based on the absorption spectrum[7] and on Coe and Lyons' method[8] of synthesis of cis-$Pd(NH_3)_2X_2$.