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Rate and Equilibrium Data for Substitution Reactions of Diaqua(ethylenediamine)palladium(II) with Chloride in Aqueous Solution

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Abstract

Kinetic and thermodynamic data are reported for the complex formation reactions.

$$Pd(en)(H_2O)_2^{2+} + Cl^- \overset{K_1}{\rightleftharpoons} Pd(en)(H_2O)Cl^+ + H_2O$$

$$Pd(en)(H_2O)Cl^+ + Cl^- \overset{K_2}{\rightleftharpoons} Pd(en)Cl_2 + H_2O$$

These species serve as models for the mechanistic behaviour of the antitumor active *cis*-$Pt(NH_3)_2Cl_2$ complex. $Pd(en)Cl_2$ undergoes spontaneous solvolysis in aqueous solution to produce $Pd(en)(H_2O)Cl^+$ and $Pd(en)(H_2O)_2^{2+}$. Spectrophotometric and potentiometric techniques were employed to determine the equilibrium constant, $K_1 = 4000$ and $K_2 = 137$ M^{-1} at 25 °C and 0.1 M ionic strength. The acid dissociation constants for the diaqua complex were found to be (pK_a) 5.6 and 7.3 under these conditions. Anation of $Pd(en)(H_2O)_2^{2+}$ by Cl^- occurs with a rate constant of 3.0×10^4 M^{-1} s^{-1}, compared to a value of 1.3×10^3 M^{-1} s^{-1} for the anation of $Pd(en)(H_2O)Cl^+$ by Cl^- at 25 °C and 0.1 M ionic strength. The kinetic data were used to determine complex formation constants, which are compared with those reported above. The results are discussed in reference to the available literature information.

Introduction

Our group has a long-standing interest in the substitution behaviour of palladium(II) complexes. Much of our earlier work was performed on diethylenetriamine (dien) and substituted dien complexes in which only one labile coordination site undergoes substitution. In this way it was possible to investigate the importance of steric hindrance on the dien ligand and its role in controlling the substitution behaviour of such complexes [1–9]. This led to a systematic study of the spontaneous solvolysis reactions of the substitution products [2], the solvent exchange reactions of the corresponding aqua complexes [8, 9], the substitution reactions at high pH [7], the solvent dependence of the solvolysis reaction [6] and leaving group effects on the solvolysis reactions [4]. In addition, the interaction of $Pd(dien)H_2O^{2+}$ and $Pd(dien)Cl^+$ with nucleic bases, nucleosides and 5′-nucleotides was studied in detail [10].

We are presently extending these studies to ethylenediamine (en) and substituted en complexes of palladium(II), in an effort to come closer to the substitution and biological behaviour of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$. In general the Pd(II) complexes are orders of magnitude more labile than the corresponding Pt(II) complexes and can therefore be studied very efficiently. The *cis*-$Pd(en)(H_2O)_2^{2+}$ complex was selected as a good model for the *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ system. In this paper we report kinetic and thermodynamic data for all the possible reactions and equilibria in the $Pd(en)(H_2O)_2^{2+}/Cl^-$ system, respectively. These studies include the application of spectrophotometric and potentiometric techniques in order to resolve all rate and equilibrium constants involved in the investigated system. The results form important background information for the interaction of these and related complexes with nucleic bases, nucleosides and 5′-nucleotides, presently under investigation in our laboratories [11].

Experimental

Materials

$Pd(en)Cl_2$ was initially synthesized according to the published procedure [12, 13]. Careful analyses indicated that a mixture of reaction products are produced under the published conditions. Better results were obtained using a procedure similar to that generally adopted to synthesize the corresponding diethylenetriamine complex. In this procedure 0.5 g $PdCl_2$ was dissolved under reflux in a mixture of 10 ml H_2O and 3 ml HCl (conc.). The clear solution was filtered and the pH was adjusted to 2–3 by the addition of NaOH. Ethylenediamine was then added dropwise to the warm solution of $PdCl_4^{2-}$ in the mole ratio 1:1. The pH of the solution

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was constantly adjusted to 2–3 by the addition of HCl. In basic medium no complex formation could be observed and irreversible hydrolysis processes interfered. If the pH is controlled carefully, a clear colour change from red to yellow is observed during the addition of the ligand. In many cases a brown–red product was isolated under these conditions, which is presumably a ring-opened species. When this product is dissolved and heated at 70 °C for 1 h, a yellow precipitate of $Pd(en)Cl_2$ is produced on cooling. *Anal.** Calc.: C, 10.1; H, 3.4; N, 11.8; Cl, 29.9. (theoretical value): Found: C, 10.5; H, 3.4; N, 11.8; Cl, 29.5%. The IR spectrum of this product in KBr was in excellent agreement with that reported in the literature [14].

The dichloro complex was converted in solution to the diaqua complex by treating $Pd(en)Cl_2$ with two equivalents of $AgClO_4$ as described before [15]. Any possible excess of Ag^+ in solution was removed by adjusting the pH to 11–12 and filtering the produced Ag_2O precipitate. The diaqua stock solution was stored at pH 2–3 to prevent eventual slow hydrolysis reactions. The solubility of the diaqua complex is significantly higher than that of the dichloro complex. All efforts to isolate the diaqua complex as a solid were unsuccessful.

Chemicals of analytical reagent grade and deionized water were used throughout this study. $NaClO_4$ was used to adjust the ionic strength of the test solutions. $HClO_4$ and NaOH were employed to adjust the pH of the test solutions.

Instrumentation

UV–Vis absorption spectra were recorded on Shimadzu UV-2100 and Hitachi U 3200 spectrophotometers. IR spectra were recorded on a Nicolet 5-SX instrument. Kinetic measurements were performed on a Durrum D 110 stopped-flow spectrophotometer coupled to a data acquisition system [16]. The studied reactions exhibited good first-order behaviour for up to three half-lives of the reaction under pseudo-first-order conditions. Equilibrium measurements were also performed potentiometrically with the aid of a WTW pMx microprocessor ion meter, an Ingold Cl^- electrode (AgS/AgCl), and a Ag/AgCl reference electrode including a NH_4NO_3 salt bridge. The latter solution was replaced daily and prevented contamination of the test solution with Cl^- ions from the 1 M KCl (saturated with AgCl) electrolyte of the reference electrode. The same system was used to measure the pH of the test solution by replacing the Cl^- electrode with a conventional glass electrode. NH_4NO_3 was used in the salt bridge instead of the usually employed KNO_3, since the latter will produce a $KClO_4$ precipitate with the ClO_4^- in the test solutions. More details on the procedure adopted with the ion selective electrode is given in the following section.

Results and Discussion

Equilibrium Studies

$Pd(en)Cl_2$ is relatively insoluble in aqueous solution, a maximum concentration of 4.3 × 10^{-3} M can be reached at 25 °C. When $Pd(en)Cl_2$ is dissolved in acidic aqueous medium it undergoes spontaneous solvolysis and produces $Pd(en)(H_2O)Cl^+$ and $Pd(en)(H_2O)_2^{2+}$. The UV–Vis spectrum of such a solution exhibits an absorption band at 355–360 nm depending on the concentration of the complex. Addition of an excess of Cl^- causes a shift to 370–372 nm (ϵ = 360 M^{-1} cm^{-1}). This band is characteristic for $Pd(en)Cl_2$ and in good agreement with that reported elsewhere [17]. The $Pd(en)(H_2O)_2^{2+}$ species exhibits a band at 340–343 nm (ϵ = 260–270 M^{-1} cm^{-1}) which gradually shifts to 370 nm on addition of Cl^- according to the complex formation reactions outlined in eqn. (1), where K_1 and K_2 are stability constants.

$$\begin{aligned} &Pd(en)(H_2O)_2^{2+} + Cl^- \underset{}{\overset{K_1}{\rightleftharpoons}} Pd(en)(H_2O)Cl^+ + H_2O \\ &Pd(en)(H_2O)Cl^+ + Cl^- \overset{K_2}{\rightleftharpoons} Pd(en)Cl_2 + H_2O \end{aligned} \qquad (1)$$

These spectra are very pH sensitive and the quoted data is valid for $2 < pH < 4$. Above pH 4, deprotonation results in the formation of hydroxo and hydroxo-bridged complexes, which is accompanied by characteristic spectral changes. A limiting spectrum with a band at 323–325 nm is reached at pH $\geqslant$ 10, which is ascribed to the formation of $(en)Pd(\mu\text{-}OH)_2Pd(en)$. Some typical UV–Vis spectra are recorded in Figs. 1 and 2, from which it follows that for a [Pd] of 1 × 10^{-3} M a 100 fold excess of Cl^- is required to form the $Pd(en)Cl_2$ complex quantitatively. The aquation products are significantly more soluble than the dichloro complex such that relatively concentrated solutions of the diaqua complex can be prepared.

Spectra similar to those reported in Fig. 2 can be used to determine the value of K_2. This was done by recording spectra of 1 × 10^{-3} M $Pd(en)Cl_2$ in 0.02, 0.03, 0.04 and 0.05 M Cl^-. Analysis of the spectral changes at 370 to 385 nm resulted in an average K_2 value of 130 ± 6 M^{-1}. The value of K_1 could not be determined spectrophotometrically due to the relatively small spectral changes on addition of low concentrations of Cl^- to $Pd(en)(H_2O)_2^{2+}$. This value could be determined potentiometrically using the Cl^- electrode (see further 'Discussion').

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*Elemental analysis carried out by Beller Mikroanalytisches Laboratorium, Göttingen, F.R.G.

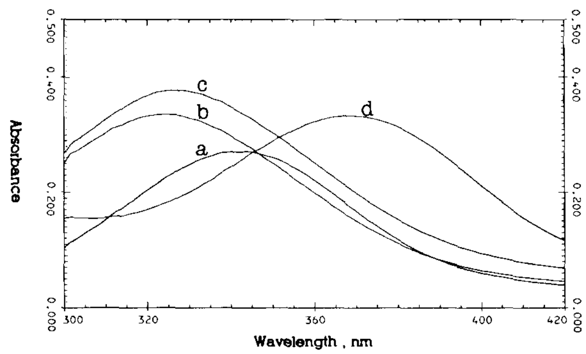

Fig. 1. UV–Vis spectra of various Pd(II) ethylenediamine complexes in aqueous solution: [Pd(II)] = 1 × 10^{-3} M; optical pathlength = 1 cm. a: $Pd(en)(H_2O)_2^{2+}$ at pH = 3, λ_{max} = 343 nm; b: $Pd(en)(H_2O)_2^{2+}$ at pH = 10, λ_{max} = 324 nm; c: $Pd(en)(H_2O)_2^{2+}$ at pH = 7, λ_{max} = 328 nm; d: $Pd(en)Cl_2$ obtained by addition of an excess Cl^- (0.025 M), λ_{max} = 368 nm.

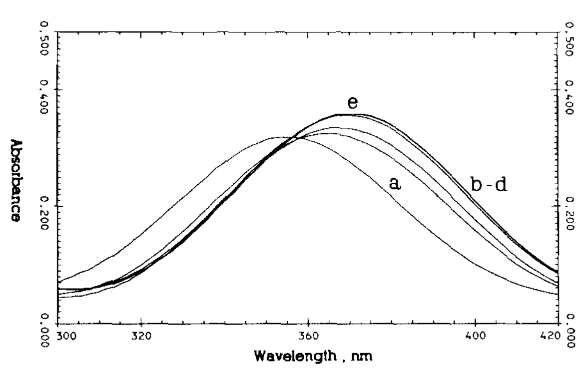

Fig. 2. UV–Vis spectra of $Pd(en)Cl_2$ recorded in different media: [Pd(II)] = 1 × 10^{-3} M; optical pathlength = 1 cm. a: Equilibrated solution of the dichloro complex dissolve in water, λ_{max} = 355 nm; b–d: Addition of 10, 20 and 50 fold excess Cl^-, respectively; e: Addition of 100 fold excess of Cl^-, λ_{max} = 370 nm (ϵ = 360 M^{-1} cm^{-1}).

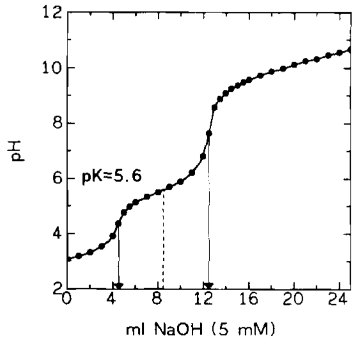

Fig. 3. pH titration of $Pd(en)(H_2O)_2^{2+}$; [Pd(II)] = 2 × 10^{-3} M; ionic strength = 0.1 M; volume of solution = 20 ml.

The diaqua complex can be titrated with base in order to determine its acid dissociation constants. A typical pH titration at 0.1 M ionic strength is given in Fig. 3, from which it follows that only a 1:1 neutralization is observed at pH < 10, the initial part of the plot being due to the presence of free acid in the diaqua stock solution (see 'Experimental'). According to the data in Fig. 3, pK_3 (eqn. (2)) has the value 5.6 at 25 °C. This value is lower than the value of 6.2 reported in the literature for a 0.2 M

$$Pd(en)(H_2O)_2^{2+} \overset{K_3}{\rightleftharpoons} Pd(en)(H_2O)OH^+ + H^+$$

$$2Pd(en)(H_2O)OH^+ \overset{K_4}{\rightleftharpoons} (en)Pd(\mu\text{-}OH)_2Pd(en) + 2H_2O \qquad (2)$$

KNO_3 solution of the complex [18], which may be due to the partial formation of a nitrate complex in the latter case. The absence of a second deprotonation step is ascribed to the direct formation of a hydroxy-bridged dimeric species for which a K_4 value of 5 × 10^3 M^{-1} was estimated [18]. The pK_a value of the $Pd(en)(H_2O)Cl^+$ species was determined in an indirect way. A solution of 1.5 × 10^{-3} M $Pd(en)Cl_2$ in 0.1 M NaCl (i.e. a 60 fold excess of Cl^-) was titrated with base. Under these conditions any aqua complex in solution will react rapidly with the excess chloride to produce the dichloro complex (see kinetic data). However, as the base concentration is increased, the spontaneous aquation product $Pd(en)(H_2O)Cl^+$ will deprotonate to produce $Pd(en)(OH)Cl$, which cannot undergo a reaction with Cl^- to produce the dichloro complex [7]. It follows that there will be a build up of the $Pd(en)(OH)Cl$ species during such a titration exactly at the pK_a value of the $Pd(en)(H_2O)Cl^+$ complex. A series of such titrations indicated a pK_a value of 7.3 ± 0.2, thus significantly higher than for the diaqua complex as expected.

The values of K_1 and K_2 can be determined accurately with the aid of the Cl^- sensitive electrode described in 'Experimental'. For this purpose the diaqua complex was treated with known quantities of Cl^-, and the free (uncoordinated) Cl^- in solution was then measured using this technique. The electrode was calibrated with standard NaCl solutions in the range 10^{-4} to 10^{-2} M Cl^- at an ionic strength of 0.1 M ($NaClO_4$). The calibration plot of electrode potential (mV) versus log[Cl^-] was linear over this concentration range with a slope of −57.2 mV, compared to a theoretical value of −59 mV under these conditions. Measurements for [total Pd(II)] = 1 × 10^{-3} M and [total Cl^-] = 1 × 10^{-4} to 1 × 10^{-3} M resulted in an average K_1 value of 4000 ± 160 M^{-1}. Similar measurements for [total Cl^-] = 6–10 × 10^{-3} M resulted in an average K_2 value of 128 ± 5 M^{-1}. The latter value was also determined by addition of chloride (6–8 × 10^{-3} M) to $Pd(en)Cl_2$ (1 × 10^{-3} M), and resulted in K_2 = 132 ± 14 M^{-1}. These values are in close agreement with those determined spectrophotometrically. The distribution of the three complexes in eqn. (1) can be presented schematically

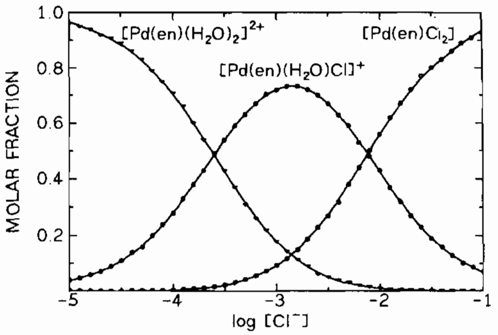

Fig. 4. Mole fractions of various Pd(II) complexes as a function of [Cl$^-$]: temperature = 25 °C, ionic strength = 0.1 M.

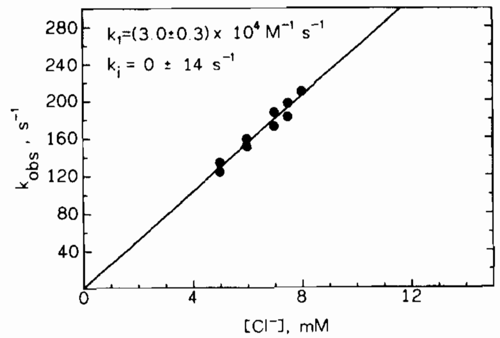

Fig. 5. k_{obs} as a function of [Cl$^-$] for the reaction Pd(en)-$(H_2O)_2{}^{2+}$ + Cl$^-$ → Pd(en)(H_2O)Cl$^+$ + H_2O: [Pd(II)] = 1 × 10^{-3} M; pH ≈ 3; ionic strength = 0.1 M; temperature = 25 °C; λ = 377 nm.

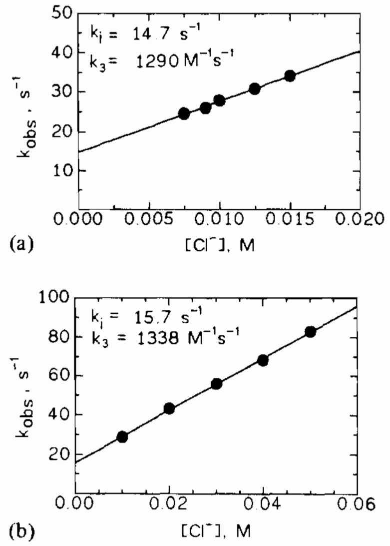

Fig. 6. k_{obs} as a function of [Cl$^-$] for the reaction Pd(en)-(H_2O)Cl$^+$ + Cl$^-$ → Pd(en)Cl_2 + H_2O. (a) Using the diaqua complex as starting material: [Pd(II)] = 1 × 10^{-3} M; pH ≈ 3; ionic strength = 0.1 M; temperature = 25 °C; λ = 377 nm. (b) Using an equilibrated solution of Pd(en)Cl_2 as starting material: [Pd(II)] = 1 × 10^{-3} M; pH ≈ 4.9; ionic strength = 0.1 M; temperature = 25 °C; λ = 377 nm.

as a function of the free [Cl$^-$] on the basis of the above K_1 and K_2 values (Fig. 4). It follows from this Figure that at a [Cl$^-$] of 10^{-3} M the main species in solution is the Pd(en)(H_2O)Cl$^+$ complex. The validity of these predictions was checked by measuring the free [Cl$^-$] as a function of [total Pd(II)] by using Pd(en)Cl_2 as starting material, and comparing the results with those predicted on the basis of K_1 = 4000 and K_2 = 130 M^{-1}. The agreement was within the experimental error limits of such measurements.

It follows from the above measurements that the stepwise stability constants follow the order $K_1 \gg K_2$. This accounts for the observation that relatively low [Cl$^-$] produces the aquachloro complex, whereas a large excess of Cl$^-$ is needed to produce the dichloro complex when starting from the diaqua complex. These effects should also clearly show up in the kinetic behaviour of these complexes.

Kinetic Studies

Anation of Pd(en)$(H_2O)_2{}^{2+}$ by Cl$^-$ results in the stepwise formation of Pd(en)(H_2O)Cl$^+$ and Pd(en)Cl_2 as summarized in eqn. (3). On mixing Pd(en)$(H_2O)_2{}^{2+}$ and Cl$^-$ in the stopped-flow instrument, two

$$\mathrm{Pd(en)(H_2O)_2{}^{2+} + Cl^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Pd(en)(H_2O)Cl^+ + H_2O} \tag{3}$$

$$\mathrm{Pd(en)(H_2O)Cl^+ + Cl^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Pd(en)Cl_2 + H_2O}$$

subsequent reactions can be observed at 377 nm. The rate constants of these reactions differ significantly such that they can easily be separated by selecting different time scales. Both reactions exhibit a linear dependence on the [Cl$^-$], and some typical results are presented in Figs. 5 and 6. The first step is extremely fast and can only be measured with large error limits due to relatively small absorbance changes at low [Cl$^-$]. A typical plot of k_{obs} versus [Cl$^-$] (Fig. 5) results in a slope k_1 = (3.0 ± 0.3) × 10^4 M^{-1} s^{-1} and an intercept k_i = 0 ± 14 s^{-1}. The value of k_1 is in close agreement with that reported in the literature [19]. The intercept represents the chloride-independent reaction path and should include k_2 (see further 'Discussion'). For the subsequent slower step the plot of k_{obs} versus [Cl$^-$] exhibits a significant intercept from which it follows that k_3 = (1.29 ± 0.04) × 10^3 M^{-1} s^{-1} and k_4 = 14.7 ± 0.5 s^{-1} (Fig. 6(a)). This reaction could also be measured starting from the Pd(en)Cl_2 complex, since the latter aquates spontaneously to produce mainly Pd(en)(H_2O)Cl$^+$ prior to mixing with Cl$^-$. The results are summarized in Fig. 6(b), from which it follows that k_3 = (1.34 ± 0.02) × 10^3 M^{-1} s^{-1} and k_4 = 15.7 ± 0.8 s^{-1}. The quoted values of k_3 and k_4 enable the estimation of K_2, which turns out to have a value (k_3/k_4) of between 85 and 88 M^{-1}, which is considerably smaller than reported in our equilibrium study above.

This discrepancy between the kinetically and thermodynamically determined values of K_2, viz. 86 ± 2 compared to 130 ± 5 M^{-1}, placed doubt on the meaning of the intercepts in Fig. 6(a) and (b). The slope of such plots can only be related to k_3, whereas the intercept k_i could arise from parallel as well as reverse reaction steps. In order to check this we measured k_4 directly by reaction the dichloro complex in the presence of an excess of chloride (0.1 M) with NaOH. Aquation of the dichloro complex (k_4) is the rate-determining step under such conditions since the reverse anation process is prevented through the deprotonation of the aqua complex in basic medium [1, 7]. The observed rate constant was independent of the NaOH concentration (0.025 to 0.05 M) and resulted in a k_4 value of 9.7 ± 1.0 s^{-1}. When this value is used to estimate K_2 (= k_3/k_4) it results in K_2 = 134 M^{-1} which is indeed close to the thermodynamically determined value. Furthermore, this result underlines that the intercepts in Fig. 6(a) and (b) represent more than only the k_4 value. Under the conditions of these experiments the only other contribution towards k_i can result from the parallel solvolysis reaction k_2, i.e. $k_i = k_2 + k_4$. Unfortunately, k_2 cannot be measured directly via the base hydrolysis reaction since we then measure the aquation of Pd(en)(Cl)OH instead of $Pd(en)(Cl)H_2O^+$. k_2 could not be determined from the intercept in Fig. 5 (see above 'Discussion'), but can be calculated from the thermodynamic value of K_1 and rate constant k_1, viz. $k_2 = k_1/K_1 = 3 \times 10^4/4000 = 7.5\ s^{-1}$. It follows that $k_i = k_2 + k_4 = 17.2\ s^{-1}$, which is rather close to the intercepts observed in Fig. 6(a) and (b).

The kinetic data show that the anation of $Pd(en)(H_2O)_2^{2+}$ by Cl^- is significantly faster than the anation of $Pd(en)(H_2O)Cl^+$, in agreement with the stability constants of the produced complexes, i.e. the values of K_1 and K_2, respectively. Our earlier studies [7] have demonstrated that hydroxo complexes of Pd(II) are substitution inert, such that an increasing pH is expected to decrease the rate of the anation reactions. This was studied by repeating the $[Cl^-]$ dependence of the reactions in eqn. (3) as a function of pH. k_3 indeed decreases significantly at pH > 4 (see Fig. 7), indicating that Pd(en)(Cl)OH is significantly less labile than the corresponding aqua complex as mentioned above. The pH dependence study could only be performed over a limited pH range due to too small spectral changes at higher pH since the reaction does not go to completion under such conditions.

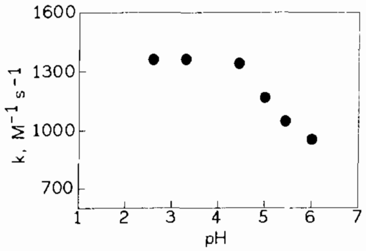

Fig. 7. k_{obs} as a function of pH for the reaction $Pd(en)(H_2O)Cl^+ + Cl^- \rightarrow Pd(en)Cl_2 + H_2O$ using the diaqua complex as starting material: [Pd(II)] = 1 × 10^{-3} M; ionic strength = 0.1 M; temperature = 25 °C; λ = 377 nm.

The results of this study once again demonstrate the importance of spontaneous solvolysis reactions and their dependence on the $[Cl^-]$ in such systems. This is of fundamental importance for the reactions of such species with nucleic bases, nucleosides and nucleotides presently under investigation in our laboratories [11]. It is furthermore of interest to compare the results of this investigation with corresponding data for the *cis*-$Pt(NH_3)_2Cl_2$ complex. For the latter complex $k_3 = 6.3 \times 10^{-3}\ M^{-1}\ s^{-1}$ and $k_4 = 6.3 \times 10^{-5}\ s^{-1}$ at 25 °C such that K_2 (= k_3/k_4) = 100 M^{-1} [20], which is close to the value of 130 M^{-1} reported here for the $Pd(en)Cl_2$ complex. It follows that although the stability constants are very similar, the significantly higher lability of the palladium complex causes the rate constants to be larger by a factor of 2 × 10^5. The corresponding value of K_1 for *cis*-$Pt(NH_3)_2Cl_2$, viz. 3700 M^{-1} [20], is also remarkably close to the value of 4000 M^{-1} reported for $Pd(en)Cl_2$.

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