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A kinetic study of the substitution behaviour of aqua and chloro complexes of ethylenediaminepalladium(II) in aqueous solution

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Abstract

Kinetic and thermodynamic data are reported for a series of substitution reactions of ethylenediamine (en) complexes of Pd(II), viz. $Pd(en)(H_2O)_2^{2+}$, $Pd(en)(Cl)H_2O^+$ and $Pd(en)Cl_2$, with iodide as entering nucleophile. All reactions exhibit two consecutive steps, of which the first involves rapid anation by iodide followed by the replacement of chloride. The kinetic data for the second step suggest the participation of a common intermediate, $Pd(en)(I)H_2O^+$, which undergoes anation by iodide with a rate constant of 122 M^{-1} s^{-1} at 25 °C. The temperature and pressure dependence of all reactions involved was studied and the corresponding activation parameters are reported. The data clearly reflect the role of steric hindrance during such substitution processes and are discussed in reference to related data reported for associative substitution reactions on square planar complexes in the literature.

Introduction

Our general interest in the substitution behaviour of palladium(II) complexes, and the important role of steric hindrance in the control of such processes, has resulted in a series of studies on diethylenetriamine (dien) and substituted dien complexes [1–7]. We have recently started to extend these studies to ethylenediamine (en) and substituted en complexes of palladium(II), where two labile coordination sites are available as compared to one in the case of the dien complexes. It is the objective of these studies to come closer to the substitution and biological behaviour of the antitumor drug *cis*-$Pt(NH_3)_2Cl_2$ and its aquation products. In general the Pd(II) complexes are orders of magnitude more labile than the corresponding Pt(II) complexes, but exhibit very similar thermodynamic behaviour in terms of stability and acid dissociation constants [8, 9].

In a recent paper [8] we reported kinetic and thermodynamic data for all the reactions and equilibria involved in the $Pd(en)(H_2O)_2^{2+}/Cl^-$ system. We have now investigated the substitution behaviour of this system with other simple nucleophiles as a first step to investigate and understand the interaction of this system with biological nucleophiles such as nucleic bases, nucleosides and 5′-nucleotides [10].

Experimental

$Pd(en)Cl_2$ was prepared and characterized as described before [8]. It was converted to the diaqua complex in solution by treatment with $AgClO_4$ [8, 11]. 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. Concentration and pH ranges were limited by the stability of the substitution products.

UV–Vis spectra were recorded on a Shimadzu UV-2100 spectrophotometer. Kinetic measurements at ambient pressure were performed on a Durrum D 110 stopped-flow spectrophotometer, whereas a homemade high pressure stopped-flow [12] was used at pressures up to 100 MPa. Both instruments were thermostated (±0.1 °C) and coupled to an on-line data acquisition system [13]. The investigated reactions were studied under pseudo-first-order conditions and exhibited good first-order behaviour for up to three half-lives of the reaction. pH measurements were performed on a WTW pMx instrument

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of which the reference electrode was filled with a 3 M NaCl solution in order to prevent the precipitation of $KClO_4$ when KCl is used as electrolyte. NMR spectra were recorded on a Bruker 400 MHz instrument.

Results and discussion

Preliminary observations

In our earlier study [8] we reported rate and equilibrium constants for the complex formation reactions outlined in eqn. (1). In this study we selected iodide as the nucleophile to react with all the species in eqn. (1), and to produce $Pd(en)I_2$ in the presence

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

$$Pd(en)(H_2O)Cl^+ + Cl^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Pd(en)Cl_2 + H_2O \qquad (1)$$

of an excess of iodide. Depending on the iodide concentration and pH selected in such experiments, the formation of $Pd(en)I_2$ was followed by a decomposition process that occurred over hours or days and produced a fine black precipitate. The decomposition reaction could be accelerated by acid and was complete in 5–10 min at $pH \approx 3$ and in 2–4 s at $pH \approx 2$. Above pH 3.8 the solutions were stable enough to enable good kinetic measurements without the interference of the decomposition process.

^1H NMR spectra of 4×10^{-3} M $Pd(en)Cl_2$ in D_2O exhibit two broad signals for the ethylene protons in the range 2.7–2.9 ppm with an intensity ratio of 1:2. These are ascribed to the symmetrical diaqua and dichloro complexes (*c*. 32 mol%) and the unsymmetrical aquachloro complexes (*c*. 65 mol%) present under these conditions (see species distribution reported in Fig. 4 of ref. 8). Addition of NaI in a 1:2 molar ratio to the complex solution resulted in a further splitting of the signals in agreement with the partial formation of iodo complexes. On addition of a large excess of NaI a single sharp signal at 2.85 ppm was formed, in agreement with the formation of $Pd(en)I_2$. Simultaneously, the addition of NaI also produced signal increases at 3.5 and 3.8 ppm, which can be assigned to the formation of ethylenediamine fragments, i.e. dechelation of the ligand. Such a decomposition is accompanied by a remarkable increase in pH presumably due to the protonation of the free chelate base. The mentioned decomposition process could also be monitored very accurately using UV–Vis detection due to the formation of the black colour (precipitate).

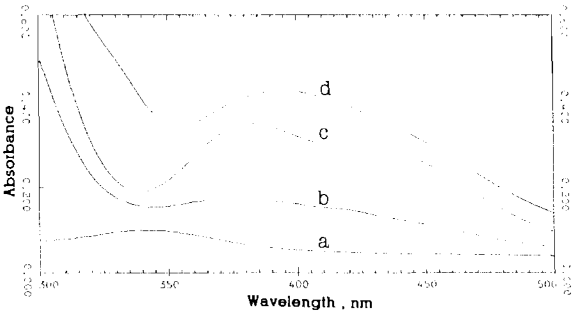


Fig. 1. UV–Vis spectra of various Pd(II)–ethylenediamine complexes in aqueous solution. Conditions: pH = 4; optical pathlength = 1 cm. (a) 2×10^{-4} M $Pd(en)(H_2O)_2^{2+}$, $\lambda_{max} = 343$ nm. (b) 1:1 mixture of 2×10^{-4} M $Pd(en)(H_2O)_2^{2+}$ and 2×10^{-4} M NaI. (c) Addition of an excess NaI to (b), $\lambda_{max} = 380$–383 and 420(sh) nm. (d) Addition of large excess of NaI to (c), $\lambda_{max} = 395$ nm.

For test solutions with pH > 5, no observable decomposition could be detected over long reaction times. We conclude that the observed decomposition must be due to a *trans*-labilization effect of coordinated iodide which results in the dechelation of the ethylenediamine ligand under conditions where the latter can be protonated to prevent the reverse chelation process. The decomposition reaction, therefore, strongly depends on the iodide concentration and pH of the test solution. We assume that the produced precipitate is PdI_2 or Pd sponge.

The UV–Vis spectrum of $Pd(en)I_2$ exhibits two bands, e.g. a broad band at 380–383 nm and a shoulder at *c*. 420 nm (Fig. 1). The band at 380 nm was selected to follow the substitution reactions studied in this investigation. In dilute solution, 1×10^{-4} M $Pd(en)(H_2O)_2^{2+}$, addition of iodide in excess results in the formation of only one broad band at 395 nm ($\epsilon = 4500$ M^{-1} cm^{-1}), which is ascribed to the formation of $Pd(en)I_2$. The two-band spectrum is observed at higher complex concentration and can be due to the formation of $Pd(en)(H_2O)I^+$. On the basis of the van der Waals radii we expect a significantly crowded and distorted situation in the $Pd(en)I_2$ complex, which may favour the stability of the $Pd(en)(H_2O)I^+$ species. We therefore expect a relatively high fraction of the aqua-iodo species in solutions that should actually mainly contain the diiodo species. Alternatively, the two bands may partially be due to the formation of a bridged complex $(en)Pd(\mu\text{-}I)_2Pd(en)^{2+}$ at high complex concentrations, similar to that reported for the Pt(II) analogue [14]. Such conditions were therefore avoided in the kinetic study.

Kinetic data

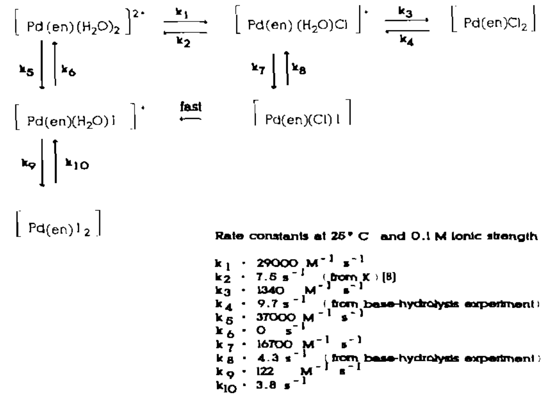
We undertook a detailed kinetic study of the reactions of the $Pd(en)(H_2O)_2^{2+}/Cl^-$ system with I^-

under conditions where no interference of the subsequent decomposition reactions of $Pd(en)I_2$ were observed (see previous section). In these studies either $Pd(en)(H_2O)_2^{2+}$ or $Pd(en)Cl_2$ in the presence of various concentrations of Cl^- or I^-, where reacted with an excess of I^-. In many cases two consecutive reaction steps could be observed, for which the rate constants differed significantly so that they could be separated for the two steps. A summary of the observed rate constants as a function of starting conditions and $[I^-]$ at ambient pressure and 25 °C is given in Table 1. The data were all fitted with eqn. (2) and the values for k_a and k_b are included

$$k_{obs} = k_a + k_b[I^-] \qquad (2)$$

in Table 1. In general such a two-term rate law can be interpreted as evidence for either two parallel reactions (one including a rate-determining step independent of $[I^-]$) or an equilibration process, i.e. a forward (k_b) and reverse (k_a) reaction step.

The results in Table 1 indicate some important trends. The very fast (first) reaction step observed on mixing $Pd(en)(H_2O)_2^{2+}$ with I^- is ascribed to the anation reaction during which $Pd(en)(H_2O)I^+$ is produced. Plots of k_{obs} versus $[I^-]$ do not exhibit a meaningful intercept within the rather large error limits involved, i.e. $k_a \approx 0$, and $k_b = (3.7 \pm 0.2) \times 10^4$ M^{-1} s^{-1}. This rate constant is very close to that reported for the corresponding anation reaction by Cl^-, viz. $(2.9 \pm 0.1) \times 10^4$ M^{-1} s^{-1} (ref. 8), although a higher rate constant is expected on the basis of the higher nucleophilicity of iodide. Steric factors in terms of the larger size of I^- may account for this observation (see further 'Discussion'). This anation reaction is also observed when $Pd(en)Cl_2$ is used as starting material since in aqueous solution a large fraction of the complex will be present in the diaqua form [8]. At $[Cl^-] = 0.01$ M the solution consists of 43% aquachloro and 56% dichloro complex, and the situation at $[Cl^-] = 0.02$ M is almost similar. It follows that the observed reaction must be due to the anation of $Pd(en)(H_2O)Cl^+$ by I^- to form Pd(en)(Cl)I. The reported values of k_b, viz. $(1.5 \pm 0.2) \times 10^3$ M^{-1} s^{-1}, are significantly smaller than those reported above for the anation of the diaqua complex by iodide. This demonstrates the difficulty encountered by I^- to enter the coordination sphere once one site is occupied by Cl^- instead of a water molecule. The observed k_a value of *c.* 11 s^{-1} is ascribed to the sum of the rate constants for the solvolysis reactions of $Pd(en)(H_2O)Cl^+$ (k_2) and Pd(en)(Cl)I (k_8 in Scheme 1). A similar assignment was made before to account for the solvolysis reactions of $Pd(en)(H_2O)Cl^+$ during the anation by Cl^- [8]. In an effort to measure the solvolysis rate constant for Pd(en)(Cl)I (k_8) directly, the base hydrolysis reaction was studied. The observed rate constant of 4.49, 4.59 and 4.83 s^{-1} at 0.016, 0.032 and 0.050 M NaOH resulted in $k_a = 4.3 \pm 0.1$ s^{-1}. Combined with the earlier reported solvolysis rate constant of 7.5 s^{-1} for $Pd(en)(H_2O)Cl^+$ (k_2) [8], it results in $k_2 + k_8 = 11.8$ s^{-1} which is close to the value of k_a observed under such conditions (see Table 1).



Rate constants at 25° C and 0.1 M ionic strength

k_1 · 29000 M^{-1} s^{-1}
k_2 · 7.6 s^{-1} (from K) [8]
k_3 · 1340 M^{-1} s^{-1}
k_4 · 9.7 s^{-1} (from base-hydrolysis experiment)
k_5 · 37000 M^{-1} s^{-1}
k_6 · 0 s^{-1}
k_7 · 16700 M^{-1} s^{-1}
k_8 · 4.3 s^{-1} (from base-hydrolysis experiment)
k_9 · 122 M^{-1} s^{-1}
k_{10} · 3.8 s^{-1}

Scheme 1.

The rate data for the second step in Table 1 are very similar and independent of starting conditions, with an average value $k_a = 3.8 \pm 0.2$ s^{-1} and $k_b = 122 \pm 8$ M^{-1} s^{-1}. Considering the variety of conditions employed to measure this reaction, the common kinetic behaviour can only be due to the participation of a common intermediate. A careful analysis of the data suggested that this species must be $Pd(en)(H_2O)I^+$, which undergoes anation to produce $Pd(en)I_2$ for which $k_b = 122 \pm 8$ M^{-1} s^{-1}. The observed intercept is ascribed to a reverse solvolysis process of the diiodo complex. The observed anation rate constant is significantly smaller than that reported for the anation of $Pd(en)(H_2O)Cl^+$ by Cl^-, viz. 1.3×10^3 M^{-1} s^{-1}, once again demonstrating the difficulty encountered by I^- to enter the coordination sphere once an iodide ligand is present. In addition, the similarity observed in the second steps suggests that even the Pd(en)(Cl)I species must aquate rapidly to follow the common reaction path, i.e. via the $Pd(en)(H_2O)I^+$ species (Scheme 1). The solvolysis rate constant of the $Pd(en)I_2$ species, viz. 3.8 s^{-1}, is significantly smaller than that of $Pd(en)Cl_2$, viz. 15.7 ± 0.8 s^{-1} [8], which can be interpreted in terms of steric hindrance and increased bond strength on the diiodo complex.

By way of comparison some reactions were performed with Br^- as anating ligand. When $Pd(en)Cl_2$ is used as starting material in the absence of added chloride, $k_{obs} = 31.1$, 41.2 and 49.6 s^{-1} for $[Br^-] = 0.004$, 0.006 and 0.008 M, respectively at 25 °C, from which it follows that $k_a = 13 \pm 1$ s^{-1} and

TABLE 1. Kinetic data for the formation of $Pd(en)I_2$ from $Pd(en)(H_2O)_2^{2+}$ and $Pd(en)Cl_2$ at 25 °C and ambient pressure[a]

Initial reaction mixture[b]	First step				Second step			
	$[I^-]$ (M)	k_{obs}[c] (s^{-1})	k_a (s^{-1})	k_b (M^{-1} s^{-1})	$[I^-]$ (M)	k_{obs}[c] (s^{-1})	k_a (s^{-1})	k_b (M^{-1} s^{-1})
[Total Pd(II)][d] = 1×10^{-4} M pH = 3.8	0.0005 0.0010 0.0015 0.0020	20 ± 2 35.3 ± 0.3 58 ± 2 74 ± 4	0.3 ± 1.0	$(3.7\pm0.2)\times10^4$	0.008 0.012 0.016 0.050	4.6 ± 0.1 5.2 ± 0.1 5.8 ± 0.2 9.8 ± 0.5	3.7 ± 0.1	120 ± 3
[Total Pd(II)][d] = 2.5×10^{-4} M $[I^-]$ = 2.5×10^{-4} M, pH = 3.8	0.002	73 ± 2[f]			0.002 0.010 0.030 0.050	4.1 ± 0.1 5.1 ± 0.2 7.8 ± 0.3 10.5 ± 0.4	3.8 ± 0.1	133 ± 2
[Total Pd(II)][d] = 2×10^{-4} M $[Cl^-]$ = 0.01 M, pH = 3.8	0.0015 0.0020 0.0025 0.0040	30 ± 2 36 ± 1 43 ± 2 61 ± 5	11 ± 1	$(12.4\pm0.4)\times10^3$	0.002 0.004 0.008 0.012 0.016	3.8 ± 0.1 4.1 ± 0.2 4.6 ± 0.1 5.2 ± 0.1 5.6 ± 0.1	3.5 ± 0.1	135 ± 5
[Total Pd(II)][d] = 5×10^{-4} M $[Cl^-]$ = 0.02 M, pH = 4.0	0.0025 0.0030 0.0035 0.0040	52 ± 3 62 ± 1 72 ± 2 77 ± 2	11 ± 5	$(16.7\pm0.2)\times10^3$				
[Total Pd(II)][e] = 1×10^{-4} M pH = 5.0	0.0005 0.0010 0.0015 0.0020	17.3 ± 0.2 34.2 ± 0.7 54 ± 2 70 ± 2	0.7 ± 1.0	$(35.6\pm0.7)\times10^3$	0.00175 0.0025 0.00375 0.0050 0.0075	4.03 ± 0.05[g] 4.17 ± 0.07[g] 4.30 ± 0.05[g] 4.5 ± 0.1[g] 4.7 ± 0.1[g]	3.86 ± 0.04	117 ± 9
[Total Pd(II)][e] = 2.5×10^{-4} M $[I^-]$ = $(2.5–5)\times10^{-4}$ M, pH = 5.0	[h]				0.0025 0.0050 0.010 0.015	4.16 ± 0.05 4.44 ± 0.05 4.99 ± 0.07 5.6 ± 0.1	3.88 ± 0.04	115 ± 5
[Total Pd(II)][e] = 2.5×10^{-4} M $[Cl^-]$ = 0.0125 M, pH = 5.0	[h]				0.004 0.005 0.010 0.015	4.31 ± 0.05 4.43 ± 0.05 5.02 ± 0.06 5.71 ± 0.06	3.79 ± 0.03	126 ± 3
[Total Pd(II)][e] = 1×10^{-4} M $[Cl^-]$ = 0.01 M, pH = 5.0	[h]				0.002 0.004 0.006 0.008	4.21 ± 0.08 4.33 ± 0.05 4.66 ± 0.07 4.92 ± 0.05	3.9 ± 0.1	123 ± 14

[a] Wavelength = 380 nm; ionic strength = 0.1 M. [b] Experimental conditions after addition of excess iodide – see 'Discussion'. [c] Mean value of at least four kinetic runs. [d] Using $Pd(en)(H_2O)_2^{2+}$ as starting complex. [e] Using $Pd(en)Cl_2$ as starting complex. [f] Measured to check reproducibility at higher [total Pd(II)]. [g] Data obtained for [total Pd(II)][e] = 2.5×10^{-4} M. [h] First step was not measured under these conditions.

TABLE 2. k_{obs} as a function of temperature and pressure for various substitution reactions of Pd(en) complexes[a]

Investigated reaction[b]	Pressure (MPa)	Temperature (°C)	[L][c] (M)	k_{obs}[d] (s^{-1})	k_a (s^{-1})	k_b ($M^{-1}\ s^{-1}$)
$R\text{-}(H_2O)_2^{2+} + I^- \rightleftharpoons R\text{-}(H_2O)(I)^+ + H_2O$	0.1	16.4	0.003	72±1	−7±10	(2.6±0.2)×10^4
[total Pd(II)] = 5×10^{-4} M, pH = 3.8			0.004	94±3		
			0.005	121±3		
		21.3	0.003	95±2	−2±4	(3.2±0.1)×10^4
			0.004	126±3		
			0.005	160±5		
		25.0[e]			0.3±1.0	(3.7±0.2)×10^4
	5	25.0	0.001[f]	32±5		
	50			36±8		
	100			41±7		
$R\text{-}(H_2O)I^+ + I^- \rightleftharpoons R\text{-}I_2 + H_2O$	0.1	12.1	0.005	1.45±0.02	1.17±0.05	46±4
[total Pd(II)] = 2.5×10^{-4} M			0.008	1.50±0.07		
			0.012	1.70±0.06		
			0.020	2.12±0.03		
		17.5	0.005	2.49±0.07	2.12±0.05	69±4
			0.008	2.67±0.04		
			0.012	2.88±0.01		
			0.020	3.52±0.04		
		21.3	0.005	3.27±0.04	2.8±0.1	106±10
			0.008	3.80±0.07		
			0.012	4.20±0.04		
			0.020	4.93±0.06		
		25.0	0.008	4.62±0.05	3.6±0.1	129±8
			0.012	5.22±0.02		
			0.016	5.77±0.04		
			0.020	6.16±0.06		
	5	24.7	0.020	6.5±0.2		
	25			7.3±0.2		
	50			8.5±0.2		
	75			9.2±0.1		
	100			11.0±0.5		
	5	23.9	0.008	4.8±0.2	[g]	[g]
			0.012	5.2±0.1		
			0.015	5.5±0.2		
	25		0.008	5.1±0.1		
			0.012	6.0±0.1		
			0.015	6.4±0.3		
	50		0.008	5.3±0.2		
			0.012	6.3±0.4		
			0.015	7.2±0.3		
	75		0.008	5.8±0.4		
			0.012	6.8±0.5		
			0.015	8.3±0.8		
	100		0.008	6.2±0.2		
			0.012	7.3±0.6		
			0.015	9.2±0.5		
$R\text{-}(H_2O)I^+ + I^- \rightleftharpoons R\text{-}I_2 + H_2O$	0.1	24.8	0.004	3.9±0.2	3.50±0.01	114±1
starting from 2×10^{-4} M $R\text{-}(H_2O)_2^{2+}$ and			0.008	4.4±0.1		
0.01 M Cl^- (see 'Discussion')			0.012	4.9±0.1		
			0.016	5.3±0.1		
		29.8	0.004	6.1±0.3	5.51±0.06	154±6
			0.008	6.7±0.1		
			0.012	7.4±0.2		
			0.016	7.9±0.2		
		34.8	0.004	8.5±0.1	7.63±0.04	227±4
			0.008	9.5±0.1		
			0.012	10.3±0.4		
			0.016	11.3±0.1		
		39.9	0.004	12.3±0.5	11.3±0.1	262±9
			0.008	13.5±0.4		
			0.012	14.5±0.5		
			0.016	15.5±0.5		

(*continued*)

TABLE 2. (*continued*)

Investigated reaction[b]	Pressure (MPa)	Temperature (°C)	[L][c] (M)	k_{obs}[d] (s^{-1})	k_a (s^{-1})	k_b (M^{-1} s^{-1})
	5	24.8	0.004	4.0±0.1	3.6±0.1	128±12
			0.008	4.7±0.1		
			0.012	5.2±0.1		
			0.016	5.6±0.1		
	25		0.004	4.6±0.2	4.0±0.2	143±17
			0.008	5.2±0.1		
			0.012	5.9±0.1		
			0.016	6.2±0.1		
	50		0.004	5.2±0.1	4.49±0.03	169±2
			0.008	5.8±0.1		
			0.012	6.5±0.1		
			0.016	7.2±0.2		
	75		0.004	5.7±0.1	5.01±0.07	193±6
			0.008	6.6±0.2		
			0.012	7.4±0.2		
			0.016	8.0±0.2		
	100		0.004	6.4±0.1	5.55±0.2	222±15
			0.008	7.5±0.1		
			0.012	8.1±0.2		
			0.016	9.1±0.2		
$R\text{-}(H_2O)Cl^+ + I^- \rightleftharpoons R\text{-}(I)Cl + H_2O$ starting from 5×10^{-4} M $R\text{-}(H_2O)_2^{2+}$ and 0.02 M Cl^- (see 'Discussion')	5	25.0	0.001	29±3		
	25			31±2		
	50			34±5		
	75			41±3		
	100			44±1		
$R\text{-}(H_2O)_2^{2+} + Cl^- \rightleftharpoons R\text{-}(H_2O)Cl^+ + H_2O$[h] [total Pd(II)] $= 1\times10^{-3}$ M, pH = 3.5, $\lambda = 370$ nm	0.1	12.4	0.005	79±7	−1±10	(1.6±0.2)×10^4
			0.006	102±16		
			0.007	113±13		
			0.008	130±11		
		18.7	0.005	111±8	−2±13	(2.3±0.2)×10^4
			0.006	138±11		
			0.007	152±6		
			0.008	182±9		
		25.0	0.005	135±12	−9±9	(2.9±0.1)×10^4
			0.006	167±9		
			0.00625	170±10		
			0.0075	204±18		
			0.008	225±12		
$R\text{-}(H_2O)Cl^+ + Cl^- \rightleftharpoons R\text{-}Cl_2 + H_2O$ [total Pd(II)] $= 1\times10^{-3}$ M, pH = 4.9, $\lambda = 370$ nm	0.1	15.0	0.0075	12±1	7.8±0.3	618±10
			0.015	16.8±0.3		
			0.025	24±1		
			0.050	38±3		
		25.0	0.010	29±1	15.7±0.8	1340±20
			0.020	43±1		
			0.030	56±1		
			0.040	68±1		
			0.050	83±3		
		35.0	0.0075	52±5	31±4	2700±150
			0.015	67±3		
			0.025	104±4		
			0.050	165±5		
	5	25.0	0.025[i]	45±4	[i]	[i]
	25			48±4		
	50			53±2		
	75			55±3		
	100			58±3		

[a] Wavelength = 380 nm; ionic strength = 0.1 M. [b] The following abbreviation is used: R = Pd(en). [c] Concentration of entering nucleophile I^- or Cl^- — see quoted reaction. [d] Mean value of at least four kinetic runs. [e] Data taken from Table 1. [f] Reaction too fast to perform concentration dependence study. [g] Absorbance changes are too small to resolve k_a and k_b accurately from k_{obs} data. [h] Reaction too fast to perform extended concentration dependence and pressure dependence studies. [i] Reaction too fast to perform concentration dependence study in high-pressure stopped-flow instrument.

TABLE 3. Rate and activation parameters for various substitution reactions of Pd(en) complexes[a]

Investigated reaction[b]	k_a at 25 °C (s^{-1})	$\Delta H_a^{\#}$ (kJ mol^{-1})	$\Delta S_a^{\#}$ (J K^{-1} mol^{-1})	$\Delta V_a^{\#}$ (cm^3 mol^{-1})	k_b at 25 °C (M^{-1} s^{-1})	$\Delta H_b^{\#}$ (kJ mol^{-1})	$\Delta S_b^{\#}$ (J K^{-1} mol^{-1})	$\Delta V_b^{\#}$ (cm^3 mol^{-1})
$R\text{-}(H_2O)_2^{2+} + I^- \rightleftharpoons R\text{-}(H_2O)I^+ + H_2O$	0.3 ± 1.0[c]				$(3.7 \pm 0.2) \times 10^4$	27 ± 1	-67 ± 4	-6.2 ± 0.5
$R\text{-}(H_2O)I^+ + I^- \rightleftharpoons R\text{-}I_2 + H_2O$ (starting from $R\text{-}(H_2O)_2^{2+}$)	3.6 ± 0.1	60 ± 5	-33 ± 16	$-6.5 \pm 0.4([I^-] = 0.008$ M) $-8.3 \pm 1.4([I^-] = 0.012$ M) $-12.9 \pm 0.9([I^-] = 0.015$ M) $-13.2 \pm 1.1([I^-] = 0.020$ M)	129 ± 8	56 ± 5	-16 ± 17	[d]
$R\text{-}(H_2O)I^+ + I^- \rightleftharpoons R\text{-}I_2 + H_2O$ (starting from $R\text{-}(H_2O)_2^{2+}$ in the presence of Cl^-)	3.50 ± 0.01	57 ± 3	-44 ± 8	-11.1 ± 0.4	114 ± 1	42 ± 5	-65 ± 17	-14.5 ± 0.3
$R\text{-}(H_2O)_2^{2+} + Cl^- \rightleftharpoons R\text{-}(H_2O)Cl^+ \ H_2O$	-9 ± 9[c]				$(2.9 \pm 0.1) \times 10^4$	29 ± 2	-61 ± 7	[e]
$R\text{-}(H_2O)Cl^+ + Cl^- \rightleftharpoons R\text{-}Cl_2 + H_2O$	15.7 ± 0.8	48.5 ± 0.5	-59 ± 2	-6.1 ± 1.0[f]	1340 ± 20	52.0 ± 0.5	-10 ± 2	[d]
$R\text{-}(H_2O)Cl^+ + I^- \rightleftharpoons R\text{-}(I)Cl + H_2O$	11 ± 5			-10 ± 1[f]	$(16.7 \pm 0.2) \times 10^3$			[d]

[a] Activation parameters were *estimated* from the data in Table 2. [b] The following abbreviation is used: R = Pd(en). [c] k_a is almost zero and too small to perform temperature and pressure dependence studies. [d] See data quoted for $\Delta V_a^{\#}$, experimental error limits did not allow a separation of k_a and k_b. [e] Reaction too fast for high-pressure stopped-flow work. [f] Measured at only one concentration of the entering nucleophile.

$k_b = (4.6 \pm 0.2) \times 10^3$ M^{-1} s^{-1}. These are assigned to a combined solvolysis/reverse step and the reaction of $Pd(en)(H_2O)Cl^+$ with Br^-, respectively. Comparison of the data with that reported for the anation of $Pd(en)(H_2O)Cl^+$ by I^- and Cl^- indicate that the trend in k_b, viz. 17 000 > 4600 > 1300 M^{-1} s^{-1} for anation by I^-, Br^- and Cl^- follows the expected nucleophilicity order. The values of k_a follow a similar sequence 15 > 13 > 11 s^{-1}, indicating that the bond strength and steric hindrance do affect the processes suggested to account for k_a, viz. solvolysis of $Pd(en)(H_2O)Cl^+$ and Pd(en)(Cl)X (X = Cl, Br, I).

The obtained kinetic data can be summarized for all the involved reactions in Scheme 1. In two cases k_a represents the sum of two rate constants as discussed above and elsewhere [8]. Remarkable is the fact that a common second step is seen under all conditions, which has been assigned to the anation of $Pd(en)(H_2O)I^+$ by I^-. This means that even in the reaction of $Pd(en)(H_2O)Cl^+$ with I^- to produce Pd(en)(Cl)I, the latter species must be very labile to produce $Pd(en)(H_2O)I^+$ for the second reaction step. This observation is presumably related to the effect of steric hindrance by the larger iodide ligand resulting in a steric 'inconvenience', as discussed earlier in this paper. A similar observation was reported for the anation reactions of diethylenetriamine complexes of Pd(II) with nucleic bases and nucleosides, where steric effects on the entering nucleophile could account for the unexpectedly slow anation reactions [2].

Activation parameters

The similarity of the observed reactions and the participation of common intermediates should also be reflected by the activation parameters ($\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta V^{\#}$) for these processes. The temperature and pressure dependences of the observed rate constants for as many as possible of the reaction steps in

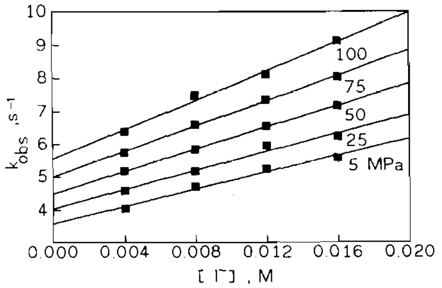


Fig. 2. k_{obs} as a function of $[I^-]$ at various pressures for the reaction of $Pd(en)(I)H_2O^+$ with I^- (see 'Discussion'). Conditions: [Pd(II)] = 2×10^{-4} M; $[Cl^-] = 0.01$ M; Temperature = 24.8 °C; pH = 4; ionic strength = 0.1 M; wavelength = 380 nm.

activation parameters are reported in Table 3. In all cases, the observed rate constants increase with increasing pressure (see Fig. 2) and plots of ln k versus pressure were linear within the experimental error limits. The volume of activation, $\Delta V^{\#}$, was calculated from the slope of these plots ($= -\Delta V^{\#}/RT$) in the usual way. It is especially this rate parameter that has in general been shown to exhibit a reliable mechanistic discrimination ability [15, 16].

All measured reactions are characterized by negative $\Delta S^{\#}$ and $\Delta V^{\#}$ values, in agreement with the associative nature of such processes [5, 7, 17]. The overall negative values are the sum of negative contributions arising from bond formation and positive contributions from charge neutralization (i.e. decrease in electrostriction) in the case of anionic entering groups. The activation parameters for k_a in principle represent those for solvolysis processes (i.e. k_2+k_4 or k_2+k_8) and involve bond formation with a solvent (water) molecule. The corresponding volumes of activation are in good agreement with those reported for related reactions elsewhere [5, 7, 17]. A comparison of the activation parameters for k_b reveals that $\Delta V^{\#}$ is significantly more negative for the anation of $Pd(en)(H_2O)I^+$ than for the formation of $Pd(en)(H_2O)I^+$, i.e. anation of $Pd(en)(H_2O)_2^{2+}$ by I^-. This is most probably due to less decrease in electrostriction in the former case in going from a singly charged species to a neutral product as compared to a 2+ and 1− species reacting to produce a 1+ species. Thus the intrinsic bond formation component plays a more important role under such conditions. The activation parameters for the anation of $Pd(en)(H_2O)I^+$ and the reaction of Pd(en)(Cl)I with I^- are very similar (especially $\Delta V^{\#}$), which also supports the operation of a common rate-determining step.

The magnitude of k_b can be correlated with the activation enthalpies, describing the effect of steric hindrance on such substitution processes. Earlier studies have clearly indicated that increasing steric hindrance can significantly increase $\Delta H^{\#}$, whereas $\Delta S^{\#}$ and $\Delta V^{\#}$ remain almost invariant [17–19]. In this way we can account for the large difference in rate constant observed for the reaction of $Pd(en)(H_2O)I^+$ and $Pd(en)(H_2O)Cl^+$ with I^- as compared to the reaction of $Pd(en)(H_2O)_2^{2+}$ with I^-.

The results of this and our earlier study [8] clearly demonstrate the kinetic complications introduced by the availability of two labile coordination sites in these complexes. It is expected that similar complications will show up in the reactions with nucleic bases, nucleosides and nucleotides presently underway in our laboratories, and also in the reactions of the related *cis*-$Pt(NH_3)_2Cl_2$, -$Pt(NH_3)(H_2O)Cl^+$ and -$Pt(NH_3)_2(H_2O)_2^{2+}$ complexes.

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References

1 M. Kotowski and R. van Eldik, *Inorg. Chem., 25* (1986) 3896.
2 E. L. J. Breet and R. van Eldik, *Inorg. Chem., 26* (1987) 2517.
3 E. l. J. Breet and R. van Eldik, *Inorg. Chem., 26* (1987) 4264.
4 M. Kotowski, S. Begum, J. G. Leipoldt and R. van Eldik, *Inorg. Chem., 27* (1988) 4472.
5 J. J. Pienaar, M. Kotowski and R. van Eldik, *Inorg. Chem., 28* (1989) 373.
6 J. J. Pienaar, M. Kotowski and R. van Eldik, *Inorg. Chim. Acta, 155* (1989) 249.
7 J. Berger, M. Kotowski, R. van Eldik, U. Frey, L. Helm and A. E. Merbach, *Inorg. Chem., 28* (1989) 3759.
8 H. Hohmann and R. van Eldik, *Inorg. Chim. Acta, 174* (1990) 87.
9 S. E. Miller and D. A. House, *Inorg. Chim. Acta, 161* (1989) 131.
10 B. Hellquist, H. Hohmann and R. van Eldik, to be published.
11 G. Mahal and R. van Eldik, *Inorg. Chem., 24* (1985) 4165.
12 R. van Eldik, D. A. Palmer, R. Schmidt and H. Kelm, *Inorg. Chim. Acta, 50* (1981) 131.
13 J. Kraft, S. Wieland, U. Kraft and R. van Eldik, *GIT Fachz. Lab., 31* (1987) 560.
14 T. V. O'Halloran, S. J. Lippard, T. J. Richmond and A. Klug, *J. Mol. Biol., 194* (1987) 705.
15 R. van Eldik (ed.), *Inorganic High Pressure Chemistry: Kinetics and Mechanisms,* Elsevier, Amsterdam, 1986.
16 R. van Eldik, T. Asano and W. J. le Noble, *Chem. Rev., 89* (1989) 549.
17 M. Kotowski and R. van Eldik, in R. van Eldik (ed.), *Inorganic High Pressure Chemistry: Kinetics and Mechanisms,* Elsevier, Amsterdam, 1986, Ch. 4.
18 R. van Eldik, E. L. J. Breet, M. Kotowski, D. A. Palmer and H. Kelm, *Ber. Bunsenges. Phys. Chem., 87* (1983) 904.
19 E. L. J. Breet and R. van Eldik, *Inorg. Chem., 23* (1984) 1865.