Hydrolysis of α-Amino-acid Esters in Mixed-ligand Complexes with 2,2′-Bipyridylpalladium(II)

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α-Amino-acid esters, $NH_2CH(R)CO_2R'$ (L), interact with $[Pd(bipy)(OH_2)_2]^{2+}$ (bipy = 2,2′-bipyridyl) in aqueous solution according to the equilibrium (i) (R and R′ = alkyl). The kinetics of hydrolysis of the ester group in the complexes $[Pd(bipy)L]^{2+}$ have been studied by pH-stat methods and rate constants have been obtained for the kinetic processes (ii) and (iii) where A = $NH_2CH(R)CO_2^-$ and L = methyl glycinate, ethyl glycinate, ethyl L-α-alaninate, ethyl L-β-phenylalaninate, ethyl picolinate, ethyl L-cysteinate, and methyl L-histidinate. For the first five esters substantial rate accelerations are observed for base hydrolysis (factors of 1.6 × 10^5 for methyl glycinate to 3.3 × 10^7 for ethyl picolinate). The effects with methyl L-cysteinate and methyl L-histidinate are much less marked, as the mixed-ligand complexes with these ligands do not involve alkoxycarbonyl donors. Possible mechanisms for these reactions are discussed, and alternative reaction schemes involving a monodentate (*N*-bonded) ester species are considered. Activation parameters have been determined for reactions (ii) and (iii) where L = methyl glycinate.

$$[Pd(bipy)(OH_2)_2]^{2+} + \overset{+}{N}H_3CH(R)CO_2R' \overset{K}{\rightleftharpoons} [Pd(bipy)\{NH_2CH(R)CO_2R'\}]^{2+} + H_3O^+ + H_2O \qquad (i)$$

$$[Pd(bipy)L]^{2+} + H_2O \xrightarrow{k_{H_2O}} [Pd(bipy)A]^+ + R'OH + H^+ \qquad (ii)$$

$$[Pd(bipy)L]^{2+} + OH^- \xrightarrow{k_{OH}} [Pd(bipy)A]^+ + R'OH \qquad (iii)$$

In a previous paper [1] we have studied the hydrolysis of a variety of amino-acid ester ligands (L) in mixed-ligand complexes with ethylenediaminepalladium(II). The mixed-ligand complex $[Pd(en)L]^{2+}$ undergoes ready hydrolysis by water and hydroxide ion. It is of considerable interest to extend this work to other palladium(II) complexes in order to define the effect of the inert ligand on the hydrolysis reaction.

Aromatic heterocycles such as 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) in addition to acting as σ-donors can also function as fairly effective π-acceptors. Thus such ligands are able to stabilise low oxidation states, and the replacement of co-ordinated water by bipy, phen, or other weak σ-donors that also have π-accepting properties usually results in an increase in E^0 due to greater stabilisation of the lower oxidation state. The use of π-acceptor ligands should thus lead to an increase in the Lewis acidity of the metal centre and more rapid hydrolysis rates.

In the case of copper(II) complexes, a variety of experiments have been designed to investigate the effects of auxiliary ligands on the ability of the metal ion to promote the hydrolysis of amino-acid esters. Both the Lewis acidity and the total charge carried by the complex are important in determining the catalytic activity. Correlations of $\lambda_{max.}$ values for tridentate copper(II) complexes have been noted with both the log of the rate constant for the copper(II) complex catalysed hydrolysis of methyl glycinate, and with the log of the formation constant for the hydroxo-complex of the copper chelate.[2]

Currently very little information is available on palladium(II) complexes, although much work has been published [3] on the hydrolysis of amino-acid ester ligands in the co-ordination sphere of metal centres such as cobalt(III), copper(II), and nickel(II).

Experimental

The complex $[Pd(bipy)Cl_2]$ was prepared as previously described.[4] The diaqua-complex $[Pd(bipy)(OH_2)_2][NO_3]_2$ was prepared in solution by stirring the chloro-complex with two mol equivalents of $AgNO_3$ overnight (with careful protection from light). The precipitated AgCl was removed by filtration and the filtrate made up to the requisite volume in a standard flask. The L-α-amino-acid ester hydrochlorides were purchased from Fluka, and converted to the corresponding hydronitrates $[\overset{+}{N}H_3CH(R)CO_2R'][NO_3^-]$ (R and R′ = alkyl) by stirring with one mol equivalent of $AgNO_3$, filtering off the precipitated AgCl, and making up to the desired volume in a standard flask. For the L-cysteine methyl ester it was necessary to prepare the hydronitrate salt from the hydrochloride by passage through an ion-exchange column (Amberlite IRA-400 in the nitrate form).

Only freshly prepared solutions were used in the kinetic studies. Ethyl picolinate (ethyl pyridine-2-carboxylate) was obtained from Koch Light and distilled before use. All other chemicals were AnalaR grade.

Kinetic Measurements.—Hydrolysis kinetics were monitored using a pH-stat. The equipment and general experimental technique employed have been outlined elsewhere.[5] The concentration of the palladium(II) complex employed was 2.23 × 10^{-4} mol dm^{-3} and the concentration of the amino-acid ester hydronitrate salt 2.25 × 10^{-4} mol dm^{-3}, in a total solution volume of 50 cm^3. It was necessary to avoid any contamination of the palladium(II) solutions with chloride ion. Leakage of chloride ion from the calomel electrode was avoided by the use of a KNO_3 salt bridge. The kinetic data were obtained as previously described;[1] all solutions were adjusted to I = 0.1 mol dm^{-3} with KNO_3. Values of the hydroxide ion concentration were obtained from the pH using pK_w = 13.997 at 25 °C and a molar activity coefficient γ_1 of 0.772. For the variable-temperature studies the following values of pK_w and γ_1 were employed:[6] at 30 °C (pK_w = 13.833, γ_1 = 0.770), at 35 °C (pK_w = 13.680, γ_1 = 0.768), and at 40 °C (pK_w = 13.535, γ_1 = 0.766). The activity coefficients were obtained using the Davies equation.[7]

Table 1. Infrared spectral data (cm^{-1}) for palladium(II) glycinate complexes

trans-[Pd(GlyO)$_2$] *	[Pd(bipy)(GlyO)][NO$_3$]$\cdot$3H$_2$O	Band assignment
1 642	1 648	ν(C=O)
1 616	1 620	δ(NH$_2$)
1 374	1 383	ν(C–O)
1 218	1 228	σ_t(NH$_2$)
771	770	σ_1(NH$_2$)
727	720	δ(C=O)

* Data taken from K. Nakamoto, ' Infrared and Raman Spectra of Inorganic and Coordination Compounds,' 3rd edn., John Wiley, New York, 1978, p. 308.

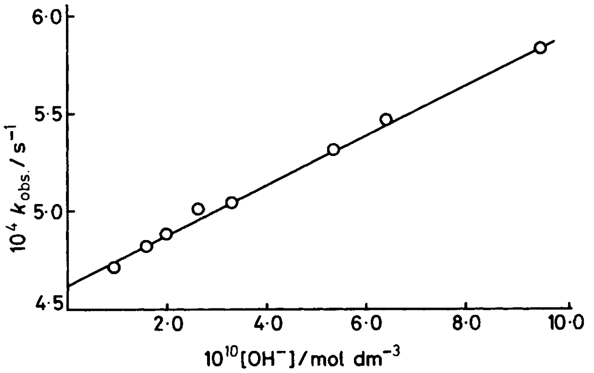


Figure. Plot of $k_{obs.}$ *versus* [OH$^-$] for the hydrolysis of [Pd(bipy)(NH$_2$CH$_2$CO$_2$Et)]$^{2+}$ at 25 °C and I = 0.1 mol dm^{-3} (KNO$_3$)

Product Analysis.—Solutions of the palladium(II) complex and glycine methyl ester hydronitrate were base-hydrolysed using the pH-stat technique outlined above but with no supporting electrolyte. The solutions resulting from some six kinetic runs were then pooled and the solvent removed on a rotatory evaporator. The resulting solid was thoroughly washed with water, then ethanol, and dried in air. The solid analysed reasonably well for the formulation [Pd(bipy)(NH$_2$CH$_2$CO$_2$)][NO$_3$]$\cdot$3H$_2$O (Found: C, 31.35; N, 12.25. Calc.: C, 31.85; N, 12.4%). The i.r. data (KBr disc), Table 1, are also in accord with this formulation. The complex has a strong band due to water at 3 400—3 500 cm^{-1} and sharp bands at 1 382, ν(NO), and 824 cm^{-1}, δ(ONO), assigned to ionic nitrate. The aromatic ring absorption ν(C=C) occurs at 1 605 cm^{-1}. The presence of co-ordinated glycinate is clearly indicated by the i.r. data summarised in Table 1.

Table 2. Kinetics of hydrolysis of the ester group in the complexes [Pd(bipy)L]$^{2+}$ at 25 °C and I = 0.1 mol dm^{-3} (KNO$_3$)

L	pH	10^{10}[OH$^-$]/ mol dm^{-3}	$10^4k_{obs.}$*/ s^{-1}
GlyOMe	3.93	1.10	5.23
	4.19	2.02	5.61
	4.35	2.92	5.83
	4.60	5.19	6.27
	5.77	7.58	6.76
	4.83	8.82	6.96
	4.94	11.36	7.46
GlyOEt	3.86	0.95	4.72
	4.09	1.60	4.82
	4.18	1.97	4.89
	4.30	2.60	5.02
	4.40	3.28	5.05
	4.61	5.31	5.32
	4.69	6.39	5.48
	4.82	9.45	5.83
L-β-PheOMe	3.06	0.15	9.07
	3.49	0.40	12.55
	3.65	0.58	14.26
	3.88	0.99	17.24
	4.05	1.46	20.72
	4.10	1.64	21.90
α-AlaOEt	4.26	2.37	7.77
	4.61	5.31	9.90
	4.80	8.23	11.11
	4.96	11.90	12.36
	5.11	16.80	13.80
	pH	10^5[OH$^-$]/ mol dm^{-3}	$10^4k_{obs.}$/ s^{-1}
L-CysOMe	9.11	1.68	3.83
	9.23	2.52	4.30
	9.33	2.79	4.93
	9.47	3.76	6.29
L-HisOMe	9.15	1.84	8.12
	9.51	4.22	9.00
	9.75	7.33	9.49
	9.89	10.13	10.03
	10.13	15.60	11.76
	pH	10^{11}[OH$^-$]/ mold dm^{-3}	$10^4k_{obs.}$/ s^{-1}
PicOEt	2.46	0.38	2.76
	2.60	0.52	2.92
	2.87	0.97	3.59
	2.97	1.22	3.96
	3.10	1.64	4.68

* Each value of $k_{obs.}$ is the average value obtained in 4 or 5 kinetic runs; the rate constants are ±0.005 s^{-1} in every case.

Results and Discussion

The reaction of the various α-amino-acid esters with [Pd(bipy)(OH$_2$)$_2$]$^{2+}$ can be summarised by equation (1). The equilibrium constant K is sufficiently large that in the pH

$$[Pd(bipy)(OH_2)_2]^{2+} + \overset{+}{N}H_3CH(R)CO_2R' \overset{K}{\rightleftharpoons} [Pd(bipy)\{NH_2CH(R)CO_2R'\}]^{2+} + H_3O^+ + H_2O \quad (1)$$

range 3—5, at a 1 : 1 ratio of palladium complex to α-amino-acid ester, formation of the mixed-ligand complex is essentially complete. Thus one mol of base is consumed per mol of the palladium complex in the pH-stat measurements. Formation of the mixed-ligand complexes with ethyl picolinate and methyl L-β-phenylalaninate is almost complete at pH 3, but for the methyl esters of L-histidine and L-cysteine a pH of 9—10 is required. Within the pH range 3—6 the hydrolysis of the unco-ordinated α-amino-acid esters is extremely slow.

Plots of log ($V_\infty - V_t$), where V_∞ is the final volume of base consumed and V_t is the volume of base consumed at time t, were linear in all cases. Values of $k_{obs.}$ (the observed first-order rate constant at constant pH) were obtained from these plots and are summarised in Table 2. Plots of $k_{obs.}$ *versus* the hydroxide ion concentration were linear with a positive intercept (Figure). The rate expression is therefore of the form $k_{obs.} = k_0 + k_{OH}[OH^-]$, the k_0 term arising from attack of water on the mixed-ligand complex. Values of $k_{H_2O} = k_0/55.5$,

Table 3. Hydrolysis data (k/dm^3 mol^{-1} s^{-1}) at 25 °C and $I = 0.1$ mol dm^{-3} (KNO$_3$)

Ester	k_{OH}	k_{H_2O}	$k_{OH}^{(ester)}$ [a]
GlyOMe	$(2.0 \pm 0.1) \times 10^5$	$(9.5 \pm 0.05) \times 10^{-6}$	1.28
GlyOEt	$(1.3 \pm 0.05) \times 10^5$	$(8.3 \pm 0.05) \times 10^{-6}$	0.63
L-CysOMe	12 ± 0.1	$(2.9 \pm 0.05) \times 10^{-6}$	0.07 [b]
L-β-PheOMe	$(7.6 \pm 0.5) \times 10^6$	$(1.8 \pm 0.2) \times 10^{-5}$	0.55
L-HisOMe	2.2 ± 0.3	$(1.4 \pm 0.05) \times 10^{-5}$	0.62
PicOEt	$(1.5 \pm 0.02) \times 10^7$	$(3.9 \pm 0.05) \times 10^{-6}$	0.46
L-α-AlaOEt	$(3.3 \pm 0.5) \times 10^5$	$(1.5 \pm 0.2) \times 10^{-5}$	0.55

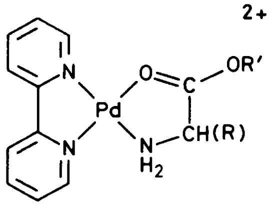
[a] Data taken from ref. 3. [b] For $^{-}SCH_2CH(NH_2)CO_2Me$.

where 55.5 mol dm^{-3} is the molar concentration of water, were determined from the intercept, and values of $k_{OH} = (k_{obs.} - k_0)/[OH^-]$ from the slope of these plots.

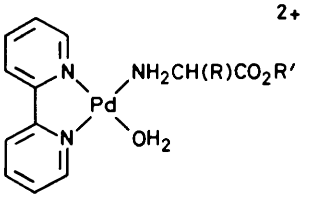
The various rate constants obtained are summarised in Table 3. Also included in the Table are the rate constants $k_{OH}^{(ester)}$ previously reported[3] for the base hydrolysis reaction, equation (2). For the α-amino-acid esters methyl

$$NH_2CH(R)CO_2R' + OH^- \xrightarrow{k_{OH(ester)}} NH_2CH(R)CO_2^- + R'OH \quad (2)$$

glycinate (GlyOMe), ethyl glycinate (GlyOEt), methyl L-β-phenylalaninate (L-β-PheOMe), ethyl picolinate (PicOEt), and ethyl L-α-alaninate (L-α-AlaOEt), the rate accelerations denoted by the rate ratio $k_{OH}/k_{OH}^{(ester)}$ are quite substantial, falling in the range 1.6×10^5 (GlyOMe) to 3.3×10^7 for PicOEt. Rate accelerations of this magnitude are fully consistent with the formulation of the mixed-ligand complex as in (I) in which there is a direct interaction between Pd^{II} and the alkoxycarbonyl group of the ester. The formation of a monodentate N-co-ordinated ester species (II) would not lead to rate accelerations of greater than *ca.* 10^2. The hydrolysis of such N-co-ordinated ester species by external nucleophiles such as hydroxide ion has been well studied in cobalt(III) systems.[8] The effect of N-co-ordination, both on the pK_a values of N-co-ordinated amino-acids and on the rates of base hydrolysis of N-co-ordinated ester, is similar to that observed on protonation of the amino-group. The formation of bidentate ester complexes with both copper(II) and cobalt(III) leads to rate accelerations[9–13] of 10^5—10^6 and the situation with palladium(II) appears to be similar. A further reaction scheme can be considered involving complex (II) in which there is intramolecular attack by co-ordinated hydroxide ion (Scheme).

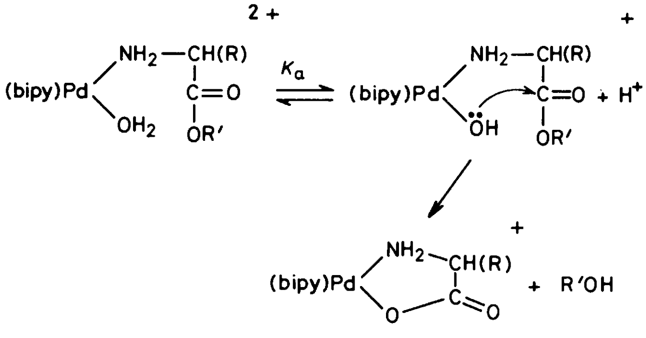


(I)



(II)

Such a mechanism requires that the pK_a of the co-ordinated water molecule in (II) is at least 6. With the exception of the histidine and cysteine esters (which can be bidentate without invoking any interaction with the alkoxycarbonyl group) the base hydrolysis was studied in the pH range 4—5. Throughout this pH range the reaction shows a first-order dependence on the hydroxide ion concentration. The intramolecular reaction would only show a hydroxide ion dependence if the pK_a of the aqua-complex was sufficiently high that the concentration of the hydroxo-complex was a linear function of the hydroxide ion concentration. Such a situation would only occur if the pK_a of the aqua-complex was at least 6 (*ca.* 10% conversion to the hydroxo-complex at pH 5). In addition it is likely[13] that such an intramolecular mechanism would lead to significantly higher rate accelerations than are observed in the present reactions. The complex $[Pd(en)(OH_2)_2]^{2+}$ is known[14] to exist as the diaqua-species at pH ⩽ 4 and $[Pd(dien)(OH_2)]^{2+}$ (dien = diethylenetriamine) has a pK_a of *ca.* 7.5.[15] Potentiometric titration of $[Pd(bipy)(OH_2)_2]^{2+}$ indicates that pK_2 is *ca.* 9. Although the pK of complexes such as (II) is unknown, it would be expected that the value would be comparable with that for $[Pd(dien)(OH_2)]^{2+}$ and so the type of intramolecular attack shown in the Scheme cannot be completely excluded. However, the rate accelerations observed suggest that there is little need to invoke the intramolecular type of mechanism to account for the present results.



Scheme. Intramolecular hydroxide ion attack

Activation parameters were determined for the hydrolysis of $[Pd(bipy)(GlyOMe)]^{2+}$ at $I = 0.1$ mol dm^{-3}. The temperature dependences of the rate constants k_{OH} and k_{H_2O} are summarised in Table 4. For k_{OH}, $\Delta H^\ddagger = 90 \pm 3$ kJ mol^{-1} and $\Delta S_{298}^\ddagger = 160 \pm 5$ J K^{-1} mol^{-1}, while for k_{H_2O}, $\Delta H^\ddagger = 25 \pm 3$ kJ mol^{-1} and $\Delta S_{298}^\ddagger = -260 \pm 5$ J K^{-1} mol^{-1}. The activation parameters for k_{H_2O} must be regarded as somewhat approximate as the requisite rate constants were determined by an extrapolation procedure. For base hydrolysis of unprotonated glycine methyl ester ($NH_2CH_2CO_2Me$) the activation parameters are[3] $\Delta H^\ddagger = 39.7$ kJ mol^{-1} and $\Delta S_{298}^\ddagger = -117$ J K^{-1} mol^{-1}. The rate acceleration in base hydrolysis arises solely due to the entropy term, as $\Delta H^\ddagger$ is considerably higher in the metal-promoted reaction. In cobalt(III) complexes it has been found that the direct polarisation mechanism involving attack of an ' external ' nucleophile such as water or hydroxide ion on a ' co-ordinated ' carbonyl group leads[9–13] to rate accelerations of 10^5—10^6 for all substrates, independent of the leaving group. In addition, the rate enhancement is due entirely to entropy factors with no contribution from the $\Delta H^\ddagger$ term.[13] A similar situation appears to occur in these Pd^{II} complexes, with the proviso that a substantial increase in $\Delta H^\ddagger$ is observed compared with the base hydrolysis of the free ligand. Intramolecular reactions of the type shown in the Scheme can lead to rate enhancements as high as 10^{11} in cobalt(III) systems,[16,17] and in this case $\Delta H^\ddagger$ factors become of great significance.

The activation parameters obtained thus lend some support to the idea that the present reactions involve hydroxide ion attack on a chelated ester species.

There are quite marked differences between the activation

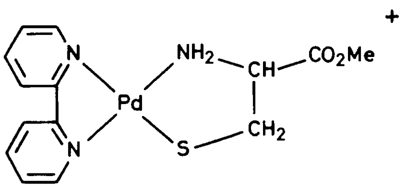
Table 4. Activation parameters for base hydrolysis and water hydrolysis of $[Pd(bipy)(NH_2CH_2CO_2Me)]^{2+}$ at $I = 0.1$ mol dm^{-3} (KNO_3) *

θ_c/°C	$10^{-5}k_{OH}$/ dm^3 mol^{-1} s^{-1}	$10^5k_{H_2O}$/ dm^3 mol^{-1} s^{-1}
25	2.0 ± 0.1	0.95 ± 0.02
30	3.50 ± 0.5	1.17 ± 0.15
35	6.69 ± 0.3	1.35 ± 0.06
40	11.73 ± 0.2	1.62 ± 0.01

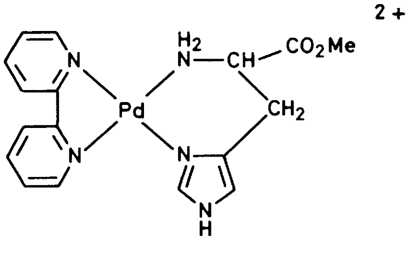
* The correlation coefficients for the least-squares analysis of the linear plots are 0.996 (25 °C), 0.999 (30 °C), 0.9997 (35 °C), and 0.996 (40 °C). For k_{OH} $\Delta H^\ddagger = 90 \pm 3$ kJ mol^{-1}, $\Delta S_{298}^\ddagger = 160 \pm 5$ J K^{-1} mol^{-1} (correlation coefficient = 0.9996); for k_{H_2O}, $\Delta H^\ddagger = 25 \pm 3$ kJ mol^{-1}, $\Delta S_{298}^\ddagger = -260 \pm 5$ J K^{-1} mol^{-1} (correlation coefficient = 0.997).

parameters for hydroxide ion and water attack, however, firm conclusions cannot be drawn from the results as activation parameters are not available for the reaction of H_2O with $NH_2CH_2CO_2Me$. Possibly there may be some initial interaction between the palladium(II) complex and hydroxide ion. This interaction may only involve the formation of a kinetically important ion pair, which should be favoured by the dipositive charge on the complex.

The relative small rate accelerations observed with methyl L-cysteinate (L-CysOMe) [$k_{OH}/k_{OH}^{(ester)} = 164$] and methyl histidinate (HisOMe) [$k_{OH}/k_{OH}^{(ester)} = 3.6$] suggest that in these cases the alkoxycarbonyl group is not bonded to the metal ion. The CysOMe complex is expected to have the structure (III) in which the donor atoms are thiolate sulphur and the α-amino-group. A similar situation (IV) is likely with HisOMe, where the α-amino-group and the pyridine nitrogen of the imidazole ring act as donors. A number of previous studies [1,18–21] have shown that the formation of such complexes with pendant ester groups leads to only relatively small rate accelerations.



(III)



(IV)

Comparative values of k_{OH} for the base hydrolysis of $[Pd(en)L]^{2+}$ and $[Pd(bipy)L]^{2+}$ complexes are listed in Table 4. For those esters in which there is believed to be a direct interaction between the metal ion and the alkoxycarbonyl group there is a small (3—5 times) rate acceleration in the $[Pd(bipy)L]^{2+}$ complexes, and there does appear to be a small, but genuine effect of the inert π-acceptor ligand. Some ' fine tuning ' of these reactions using different inert ligands is thus possible. Little formation constant data are available for Pd^{II} amine complexes. For the palladium(II)–ethylenediamine system a value of log $\beta_2 = 26.90$ has been reported,[22] but there appear to be no analogous data for the palladium(II)–bipyridyl system. For nickel(II) the requisite formation constants are, for bipy log $K_1 = 7.13$ and log $K_2 = 6.88$, and for en log $K_1 = 7.52$ and log $K_2 = 6.11$ at 20 °C.[22] The quite comparable formation constants would also suggest that the catalytic effects of the two Pd^{II} complexes would not be markedly different since the Lewis acidity of the metal centres will be quite similar.

Table 5. Comparative values of k_{OH} (dm^3 mol^{-1} s^{-1}) for the base hydrolysis of the complexes $[Pd(en)L]^{2+}$ and $[Pd(bipy)L]^{2+}$ at 25 °C

L	k_{OH}- $\{[Pd(en)L]^{2+}\}$	k_{OH}- $\{[Pd(bipy)L]^{2+}\}$	$\dfrac{k_{OH}\{[Pd(en)L]^{2+}\}}{k_{OH}\{[Pd(bipy)L]^{2+}\}}$
GlyOMe	6.3×10^4	2.0×10^5	3.2
GlyOEt	2.5×10^4	1.3×10^5	5.2
L-α-AlaOEt	6.2×10^4	3.3×10^5	5.3
HisOMe	12.8	2.2	0.2
PicOEt	6.5×10^6	1.5×10^7	2.3

Attack of water on the $[Pd(bipy)L]^{2+}$ complexes as determined by the k_{OH}/k_{H_2O} ratios is some 2×10^{10} slower than that of hydroxide ion. Such a value for the relative nucleophilicity of hydroxide ion and water is very comparable with the data obtained for $[Pd(en)L]^{2+}$ complexes [1] and for a variety of copper(II) complexes.[23] Hydroxide ion does have a somewhat higher reactivity towards[$Pd(en)(PicOEt)]^{2+}$, with $k_{OH}/k_{H_2O} = 3.8 \times 10^{12}$.

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References

1 R. W. Hay and P. Banerjee, *J. Chem. Soc., Dalton Trans.*, 1981, 362.
2 J. K. Walker and R. Nakon, *Inorg. Chim. Acta*, 1981, **55**, 135.
3 For a review see, R. W. Hay and P. J. Morris, in ' Metal Ions in Biological Systems,' ed. H. Sigel, Marcel Dekker, New York, 1976, vol. 5, p. 173.
4 J. L. Burmeister and F. Basolo, *Inorg. Chem.*, 1964, **3**, 1587; G. T. Morgan and F. H. Burstalli, *J. Chem. Soc.*, 1934, 965.
5 R. W. Hay, L. J. Porter, and P. J. Morris, *Aust. J. Chem.*, 1966, **19**, 1197.
6 R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' 2nd edn., Butterworths, London, 1979.
7 C. W. Davies, *J. Chem. Soc.*, 1936, 2093.
8 R. W. Hay, R. Bennett, and D. P. Piplani, *J. Chem. Soc., Dalton Trans.*, 1978, 1046; R. W. Hay, R. Bennett, and D. J. Barnes, *ibid.*, 1972, 1524.
9 M. D. Alexander and D. H. Busch, *J. Am. Chem. Soc.*, 1968, **88**, 1130.
10 D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Am. Chem. Soc.*, 1968, **90**, 6032.
11 D. A. Buckingham, D. M. Foster, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 1970, **9**, 11.
12 D. A. Buckingham, J. M. Harrowfield, and A. M. Sargeson, *J. Am. Chem. Soc.*, 1974, **96**, 1726.
13 C. J. Boreham, D. A. Buckingham, and F. R. Keene, *Inorg. Chem.*, 1979, **18**, 28.
14 M. C. Lim, *J. Chem. Soc., Dalton Trans.*, 1977, 15.

15 M. C. Lim, *J. Inorg. Nucl. Chem.*, 1981, **43**, 221.
16 D. A. Buckingham, P. J. Morris, A. M. Sargeson, and A. Zanella, *Inorg. Chem.*, 1977, **16**, 1910.
17 D. A. Buckingham, A. M. Sargeson, and A. Zenella, *J. Am. Chem. Soc.*, 1972, **94**, 8246.
18 R. W. Hay and L. J. Porter, *J. Chem. Soc. A*, 1969, 127.
19 R. W. Hay and P. J. Morris, *J. Chem. Soc. A*, 1971, 1525.
20 R. W. Hay and P. J. Morris, *J. Chem. Soc., Dalton Trans.*, 1973, 56.
21 R. W. Hay and P. Banerjee, *Inorg. Chim. Acta*, 1980, **44**, L205·
22 ' Stability Constants of Metal-Ion Complexes,' eds. L. G. Sillen and A. E. Martell, Chemical Society, London, 1964, and 1st supplement.
23 R. W. Hay and K. B. Nolan, *J. Chem. Soc., Dalton Trans.*, 1975, 1348.

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