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The Palladium(II) Promoted Hydrolysis of Methyl, Ethyl and Isopropyl Glycylglycylglycinate

ROBERT W. HAY and MAHESH P. PUJARI

Chemistry Department, University of Stirling, Stirling, FK9 4LA, U.K.

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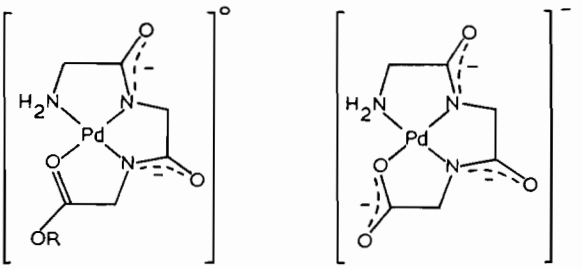
Abstract

The palladium(II) promoted hydrolysis of the ester function of methyl, ethyl and isopropyl glycylglycylglycinate has been studied in detail in the pH range 4–5. The tripeptide esters interact with $[PdCl_4]^{2-}$ at a 1:1 metal-to-ligand ratio to give the complex **I** in which the α-amino group, two deprotonated amide nitrogen atoms and the alkoxy carbonyl group of the ester act as donors. Rate constants have been determined for hydrolysis of the ester function by water and hydroxide ion and activation parameters obtained for the hydrolysis of the methyl ester. At 25 °C base hydrolysis of the coordinated ester is 10^6 fold that of the free ester ligand. Mechanisms for the reactions are considered.

Introduction

The metal ion promoted hydrolysis of esters and peptides has attracted considerable attention due to the relevance of these systems to the function of metalloenzymes. Aspects of the topic have been reviewed [1, 2]. At pH 4 dipeptides form a tridentate chelate about palladium(II) consisting of two five-membered rings with amino, deprotonated amide, and carboxylato–oxygen donor atoms [3]. We have previously shown that dipeptide esters also act as tridentate ligands, donation occurring via the terminal amino group, the deprotonated amide nitrogen and the alkoxycarbonyl group of the ester [4]. As a result of the interaction of the alkoxycarbonyl group with Pd(II), base hydrolysis of the coordinated ester is *ca.* 10^5 times faster than the free unprotonated peptide esters. In the present work we have extended out investigations to tripeptide esters. Esters of triglycine should form the tetradentate complex **I** which would be expected to undergo nucleophilic attack by both hydroxide ion and water to give the triglycine complex **II**. Tripeptide ligands form planar complexes with Pd(II) coordinated at the amino group, two deprotonated peptide nitrogens, and the carboxylate group [3]. Palladium(II) has many attractive features as a Lewis acid due to:



I **II**

R = Me, Et, Pr^i

(a) its fixed coordination number of four, (b) its high Lewis acidity; the $[Pd(H_2O)_4]^{2+}$ ion being square planar is much more acidic ($pK_a = -2.3$) than octahedrally coordinated divalent ions such as $[Zn(H_2O)_6]^{2+}$ ($pK_a = 8.96$). $[Co(H_2O)_6]^{2+}$ ($pK_a = 9.65$) and $[Cu(H_2O)_6]^{2+}$ ($pK_a = 7.96$) [5], (c) its high formation constants with N, O donor ligands and (d) its intermediate kinetic lability.

Experimental

Glycylglycylglycine was obtained from Fluka. Methyl glycylglycylglycinate hydrochloride was prepared as follows. To ice-cold methanol (250 cm^3) was added thionyl chloride (2.5 g, excess) dropwise with constant stirring at such a rate that the temperature was always less than *ca.* 5 °C. Triglycine (2 g) was then added and the solution refluxed for 4 h. The bulk of the solvent was removed on a rotary evaporator to leave a solution volume of *ca.* 25 cm^3. Addition of dry diethyl ether precipitated the ester hydrochloride as an oil, which on cooling to −10 °C and scratching gave a white crystalline solid which was filtered off and recrystallised from methanol–ether. The ester was air dried (yield 1.6 g). *Anal.*: Calc. for $C_7H_{14}N_3O_4Cl$: C, 35.08; H, 5.89; N, 17.53. Found: C, 35.13; H, 5.77; N, 17.73%.

A similar procedure was used for the ethyl ester using triglycine (0.9 g), thionyl chloride (1.25 g) and ethanol (150 cm^3). In this case addition of diethyl ether gave a white crystalline solid on cooling

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which was recrystallised from ethanol–ether (yield 0.85 g). *Anal.*: Calc. for $C_8H_{16}N_3O_4Cl$: C, 37.88; H, 6.36; N, 16.56. Found: C, 37.59; H, 6.23; N, 16.34%.

The isopropyl ester was prepared using triglycine (0.9 g), thionyl chloride (1.25 g) and isopropanol (150 cm^3). Addition of diethyl ether gave the crystalline ester hydrochloride which was recrystallised from isopropanol–ether. *Anal.*: Calc. for $C_9H_{18}N_3O_4Cl$: C, 40.38; H, 6.78; N, 15.70. Found: C, 40.24; H, 6.86; N, 15.81%.

Kinetics

All kinetic measurements were carried out using a Radiometer TTT2 automatic titrator used as a pH-stat. A high-alkalinity glass electrode type G202B was used as indicator electrode, and a saturated calomel electrode with diffusion filter, type K401 as reference electrode. The electrode system was standardised at 25 ± 0.1 °C using 0.05 mol dm^{-3} potassium hydrogen phthalate (pH 4.008) and 0.01 M disodium tetraborate (pH 9.185). At the other temperatures the recommended pH standards were employed [6]. The general technique employed in the kinetic measurements has been outlined previously [7]. All pH-stat studies were carried out at $I = 0.1$ M ($NaClO_4$) with methyl, ethyl or isopropyl glycylglycylglycinate hydrochloride (2.25×10^{-4} M) and $K_2[PdCl_4]$ (2.25×10^{-4} M). 1 mol of base was consumed per mol of the ester in the pH-stat measurements. Values of the hydroxide ion concentration were obtained from the pH using a molar activity coefficient y_1 of 0.772 [8] and a value of pK_w = 13.997 at 25 °C [9]. At the other temperatures the appropriate values are $y_1 = 0.770$, $pK_w = 13.833$ (30 °C); $y_1 = 0.768$, $pK_w = 13.680$ (35 °C); and $y_1 = 0.766$, $pK_w = 13.535$ (40 °C).

For the potentiometric titrations the solutions used were 1×10^{-3} M in both $K_2[PdCl_4]$ and the ligand (methyl glycylglycylglycinate hydrochloride on triglycine); $I = 0.1$ M ($NaClO_4$) and 25 °C. In this case the pH measurements were made with a Radiometer PHM 64 Research pH-meter.

Results and Discussion

Potentiometric titration of a 1:1 molar mixture of $K_2[PdCl_4]$ with triglycine indicates the release of three protons, Fig. 1, a, from the protonated amino group and from deprotonation of two peptide bonds. Analogous behaviour is shown by a 1·1 molar mixture of $K_2[PdCl_4]$ and methyl triglycinate, Fig. 1, b. Hydrolysis of the ester ligand occurs in the pH range 4–5 1 mol of base is consumed per mol of the ester on hydrolysis in the presence of 1 mol equivalent of $K_2[PdCl_4]$ in this pH range. The kinetics of hydrolysis of the methyl ester were

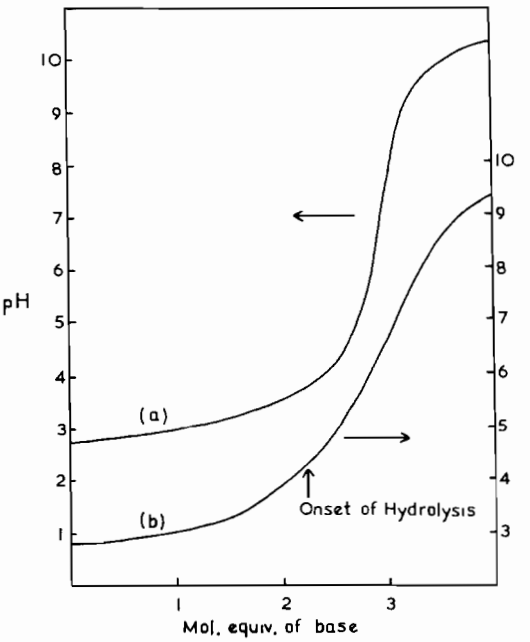


Fig. 1 (a) Potentiometric titration of a 1 1 mixture (1×10^{-3} M) of $K_2[PdCl_4]$ and glycylglycylglycine at 25 °C and $I = 0.1$ M ($NaClO_4$), (b) potentiometric titration of a 1·1 mixture (1×10^{-3} M) of $K_2[PdCl_4]$ and methyl glycylglycylglycinate hydrochloride at 25 °C and $I = 0.1$ M ($NaClO_4$).

monitored by pH-stat over the pH range 4.06–4.82 at 25 °C and $I = 0.1$ M. Values of k_{obs} (the observed first-order rate constant at constant pH) for the hydrolysis of the methyl ester are summarised in Table I at various temperatures. A plot of k_{obs} *vs.* $[OH^-]$ is linear with a positive intercept, Fig. 2. The kinetic data conform to the equation $k_{obs} = k_o + k_{OH}[OH^-]$ Least-square analysis of the data at 25 °C gives $k_o = 1.49 \times 10^{-3}$ s^{-1} and $k_{OH} = 2.49 \times 10^6$ M^{-1} s^{-1} at $I = 0.1$ M. Values of k_o (which arise due to water attack on the ester ligand) were converted to k_{H_2O} rate constants $k_{H_2O} = k_o/55.5$, where 55.5 M is the molar concentration of water, giving $k_{H_2O} = 2.68 \times 10^{-5}$ M^{-1} s^{-1} at 25 °C. The ratio $k_{OH}/k_{H_2O} = 9.3 \times 10^{10}$ and is of the expected order of magnitude (10^{10}–10^{11} fold) for the relative nucleophilicities of hydroxide ion and water for reactions of this type [10]. The rate constants k_{OH} and k_{H_2O} at various temperatures are summarised in Table II. The requisite activation parameters are $\Delta H^{\ddagger} = 92.8 \pm 1$ kJ mol^{-1} and $\Delta S^{\ddagger}_{298} = -21 \pm 3$ JK^{-1} mol^{-1} (for k_{H_2O}) and $\Delta H^{\ddagger} = 82.6 \pm 7$ kJ mol^{-1} and $\Delta S^{\ddagger}_{298} = 153 \pm 25$ JK^{-1} mol^{-1} (for k_{OH}). These values are very comparable with those previously obtained [4] for the Pd(II) promoted hydrolysis of methyl glycylglycinate. Values of $\Delta H^{\ddagger}$ are somewhat higher for H_2O attack than for attack by hydroxide ion, and the major rate difference

TABLE I. Hydrolysis of the 1:1 Complex of Methyl Glycylglycylglycinate with Palladium(II) at Various Temperatures and I = 0.1 M ($NaClO_4$)[a]

Temperature (°C)	pH	10^{10} [OH^-] (M)	$10^3 k_{obs}$ (s^{-1})
25	4.06	1.50	1.84
	4.14	1.80	1.93
	4.21	2.12	2.03
	4.46	3.76	2.43
	4.51	4.23	2.58
	4.68	6.25	3.07
	4.82	8.63	3.62
30	3.78	1.15	3.12
	3.90	1.51	3.27
	4.05	2.14	3.50
	4.28	3.64	4.05
	4.48	5.76	4.77
35	3.89	2.11	6.64
	4.07	3.19	7.29
	4.23	4.62	8.61
	4.33	5.82	9.24
	4.42	7.15	10.15
40	3.64	1.66	11.39
	3.75	2.14	11.99
	3.84	2.64	12.59
	3.91	3.09	13.05
	3.95	3.39	13.60

[a]Tripeptide ester 2.25 × 10^{-4} M, $K_2[PtCl_4]$ 2.25 × 10^{-4} M.

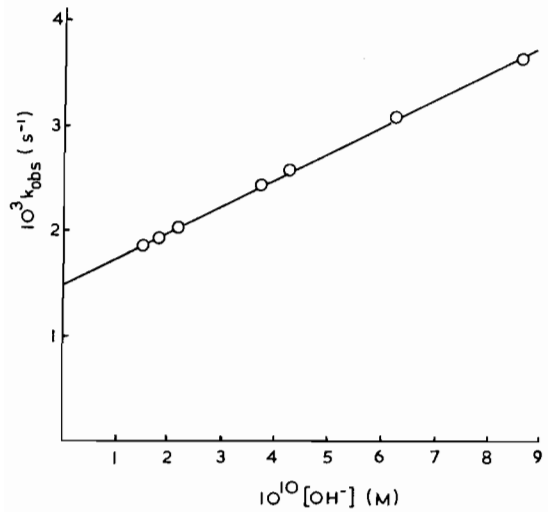


Fig. 2. Plot of k_{obs} *vs.* [OH^-] for the hydrolysis of the ester function of the 1:1 complex of methyl glycylglycylglycinate with palladium(II) at 25 °C and I = 0.1 M ($NaClO_4$).

between the two nucleophiles is due primarily to a more positive value of $\Delta S^{\ddagger}$ for attack by hydroxide ion. Analogous measurements were carried out with ethyl- and isopropyl glycylglycylglycinate, Table III.

TABLE II. Derived Constants and Activation Parameters for the Palladium(II) Promoted Hydrolysis of Methyl Glycylglycylglycinate at I = 0.1 M ($NaClO_4$)

Temperature (°C)	$10^5 k_{H_2O}$[a] ($M^{-1} s^{-1}$)	$10^{-6} k_{OH}$ ($M^{-1} s^{-1}$)	r[b]
25	2.68 ± 0.03	2.49 ± 0.04	0.9994
30	4.92 ± 0.04	3.57 ± 0.05	0.9996
35	9.28 ± 0.04	7.07 ± 0.3	0.9966
40	16.81 ± 0.25	12.36 ± 0.53	0.9972

[a]$k_{H_2O} = k_o/55.5$. [b]r is the correlation coefficient of the linear plot of k_{obs} *vs.* [OH^-]. For k_{H_2O}, $\Delta H^{\ddagger}$ = 92.8 ± 1 kJ mol^{-1} and $\Delta S^{\ddagger}_{298}$ = −21 ± 3 JK^{-1} mol^{-1} (r = 0.999). For k_{OH}, $\Delta H^{\ddagger}$ = 82.6 ± 7 kJ mol^{-1} and $\Delta S^{\ddagger}_{298}$ = 153 ± 25 JK^{-1} mol^{-1} (r = 0.992).

TABLE III. Hydrolysis of the 1:1 Complexes of Ethyl and Isopropyl Glycylglycylglycinate with Palladium(II) at 25 °C and I = 0.1 M ($NaClO_4$)[a]

Ester	pH	10^{10} [OH^-] (M)	10^3 k_{obs} (s^{-1})
Ethyl	4.22	2.17	1.28
	4.42	3.43	1.54
	4.51	4.23	1.68
	4.61	5.32	1.90
	4.71	6.69	2.22
Isopropyl	3.98	1.25	0.96
	4.19	2.02	1.06
	4.24	2.27	1.12
	4.46	3.76	1.24
	4.81	9.03	1.95

[a]For the ethyl ester k_{H_2O} = (1.49 ± 0.05) × 10^{-5} M^{-1} s^{-1} and k_{OH} = (2.05 ± 0.05) × 10^6 $M^{-1} s^{-1}$ (r = 0.9989). For the isopropyl ester k_{H_2O} = (1.44 ± 0.04) × 10^{-5} M^{-1} s^{-1} and k_{OH} = (1.26 ± 0.05) × 10^6 $M^{-1} s^{-1}$ (r = 0.998).

The various derived rate constants are summarised in Table IV. The base hydrolysis of alkyl esters normally follows the order Me > Et > Pr^i [1] and a similar trend is observed with the metal complexes. Values of k_{OH}/k_{H_2O} are *ca.* 10^{11} fold in all cases.

The base hydrolysis of uncomplexed methyl glycylglycylglycinate was studied over a temperature range (25–40 °C) in order to assess the rate accelerations in the Pd(II) promoted reaction and to determine the requisite activation parameters for hydrolysis of the free ligand. The ionisation equilibria of the triglycine ester can be represented,

$$\overset{+}{N}H_3glyglyglyOMe \overset{K_a}{\rightleftharpoons} NH_2glyglyglyOMe + H^+$$

EH^+ E

where pK_a is *ca.* 7.5. Base hydrolysis was studied in the pH range 10 to 11 where hydrolysis of the un-

TABLE IV. Derived Rate Constants for the Palladium(II) Promoted Hydrolysis of Methyl, Ethyl and Isopropyl Glycylglycylglycinate at 25 °C and I = 0.1 M ($NaClO_4$)

Ester	k_{OH} (M^{-1} s^{-1})	k_{H_2O} (M^{-1} s^{-1})	k_{OH}/k_{H_2O}
Methyl	2.49×10^6	2.68×10^{-5}	9.3×10^{10}
Ethyl	2.05×10^6	1.49×10^{-5}	1.4×10^{11}
Isopropyl	1.26×10^6	1.44×10^{-5}	8.8×10^{10}

TABLE V. Kinetics of Base Hydrolysis of Methyl Glycylglycylglycinate at Various Temperatures and I = 0.1 M (KNO_3)

Temperature (°C)	pH	10^4 [OH^-] (M)	$10^3 k_{obs}$ (s^{-1})	k_{OH} (M^{-1} s^{-1})
25	10.08	1.57	0.24	1.53
	10.19	2.02	0.30	1.48
	10.68	6.25	0.96	1.54
	10.71	6.69	1.04	1.55
	10.78	7.87	1.17	1.49
	10.83	8.83	1.34	1.52
30	9.90	1.51	0.30	1.98
	9.98	1.82	0.35	1.92
	10.14	2.63	0.52	1.97
	10.26	3.47	0.66	1.90
	10.49	5.89	1.21	2.05
	10.54	6.61	1.28	1.93
	10.69	9.34	1.77	1.89
	10.76	10.97	2.13	1.94
35	9.89	2.11	0.54	2.56
	9.97	2.54	0.66	2.59
	10.23	4.62	1.15	2.49
	10.36	6.23	1.58	2.54
	10.41	6.99	1.82	2.60
	10.52	9.00	2.25	2.50
40	9.94	3.32	1.10	3.31
	10.17	5.64	1.90	3.37
	10.23	6.47	2.15	3.32
	10.34	8.34	2.83	3.39
	10.59	14.82	4.89	3.30

TABLE VI. Rate Constants and Activation Parameters for the Base Hydrolysis of Methyl Glycylglycylglycinate at I = 0.1 M (KNO_3)[a]

Temperature (°C)	k_{OH} (M^{-1} s^{-1})
25	1.52 ± 0.03
30	1.95 ± 0.05
35	2.55 ± 0.04
40	3.34 ± 0.05

[a] $\Delta H^{\ddagger}$ = 38.3 ± 1 kJ mol^{-1}; $\Delta S^{\ddagger}_{298}$ = −113 ± 3 JK^{-1} mol^{-1}; the correlation coefficient (r) of the Eyring plot is 0.9994.

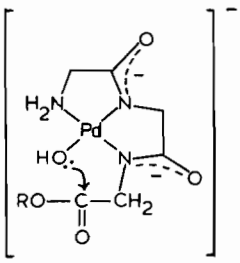
protonated ester E is the only kinetically significant process. The rate constants obtained are summarised in Table V. Values of $k_{OH} = k_{obs}/[OH^-]$ are quite constant within the pH range used for the measurements, giving k_{OH} = 1.52 ± 0.03 M^{-1} s^{-1} at 25 °C. This rate constant is very similar to that previously determined for the base hydrolysis of methyl glycinate [11], where k_{OH} = 1.28 M^{-1} s^{-1} at 25 °C and I = 0.1 M. The rates of base hydrolysis of peptide esters appear to be very comparable with those for the analogous ester of the C-terminal amino-acid. The rate constant k_{OH} = 1.52 M^{-1} s^{-1} may be compared with $k_{OH} = 2.49 \times 10^6$ M^{-1} s^{-1} for base hydrolysis of methyl triglycinate in the Pd(II) complex. At 25 °C the rate acceleration is 1.7×10^6 fold.

For the base hydrolysis of methyl triglycinate the activation parameters are $\Delta H^{\ddagger}$ = 38.3 ± 1 kJ mol^{-1} and $\Delta S^{\ddagger}_{298}$ = −113 ± 3 JK^{-1} mol^{-1}, Table VI. These values are almost identical to those previously reported [11] for the base hydrolysis of methyl glycinate where $\Delta H^{\ddagger}$ = 39.7 kJ mol^{-1} and $\Delta S^{\ddagger}_{298}$ = −117 JK^{-1} mol^{-1}. Substantial negative entropies of activation are expected in a bimolecular reaction of this type. In the Pd(II) promoted base hydrolysis of methyl triglycinate $\Delta H^{\ddagger}$ = 82.6 ± 7 kJ mol^{-1} and $\Delta S^{\ddagger}_{298}$ = 153 ± 25 JK^{-1} mol^{-1}. Values of $\Delta H^{\ddagger}$ are considerably higher in the Pd(II) promoted reaction than for the free ligand. The rate acceleration of 10^6 fold arising exclusively from the much more positive entropy of activation. Analogous results have been obtained in the Pd(II) promoted hydrolysis of methyl glycylglycinate where $\Delta H^{\ddagger}$ = 78.7 kJ mol^{-1} and $\Delta S^{\ddagger}_{298}$ = 118 JK^{-1} mol^{-1} [4]. Table VII summarises the available kinetic data on the hydrolysis of amino acid ester and peptide ester ligand in Pd(II) complexes. The rate acceleration in base hydrolysis arises solely due to the entropy term in all the reactions studied. Values of $\Delta H^{\ddagger}$ 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 'coordinated' carbonyl group leads [2, 12] to rate accelerations of 10^5 to 10^6 fold 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 [12]. 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.

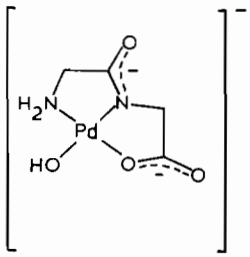
In addition to the direct polarisation mechanism involving Lewis acid catalysis in the complex **I**, a further reaction scheme can also be considered in which base hydrolysis occurs via intramolecular attack by coordinated hydroxide in a complex of type **(III)**. Previous investigations [13] have shown

TABLE VII. Rate Constants and Activation Parameters for the Base Hydrolysis of Amino Acid Ester and Peptide Ester Ligands in Pd(II) Complexes at $I = 0.1$ M

Complex	k_{OH}^{25} (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}_{298}$ (JK^{-1} mol^{-1})	Reference
$[Pd(glyglyOMe)OH_2]^+$	1.55×10^5	78.7	118	4
$[Pd(glyglyglyOMe)]^0$	2.5×10^6	82.6 ± 7	153 ± 25	This work
$[Pd(en)(glyOMe)]^{2+}$	6.2×10^4			17
$[Pd(bipy)(glyOMe)]^{2+}$	2×10^5	90 ± 3	160 ± 5	16
$[Pd(piperidine)_2(glyOMe)]^{2+}$	3.7×10^5	87.7 ± 2	156 ± 5	18
glyOMe	1.28	39.7	−117	11
glyglyglyOMe	1.52	38.3	−113	This work



III



IV

that Pd(II)–dipeptide complexes do not form hydroxo species **IV** until pH 8. As a result, it is expected that hydroxo species of Pd(II)–tripeptide esters **III** would only exist in significant concentrations at pH > 8, since **III** and **IV** are of a similar charge type. Hydrolysis of the Pd(II)–tripeptide ester complexes was studied in the pH range 4–4.8 at 25 °C, where the absolute concentration of the hydroxo species will be insignificant, although it could have kinetic significance. The intramolecular reaction would show an hydroxide ion dependence if the pK_a of the aquo-complex was sufficiently high that the concentration of the hydroxo-complex was a linear function of the hydroxide ion concentration. This situation would occur if the pK_a of the aquo complex was >6. In principle the two mechanisms could be differentiated by measurements at high pH, but unfortunately this is not practical using the pH stat technique as the reactions would be too rapid to monitor by this method.

Although the kinetic measurements do not directly distinguish between the two possible mechanisms, other evidence strongly suggests that base hydrolysis occurs by hydroxide ion attack on the carbonyl bonded complex (**I**). The rate accelerations of 10^5 to 10^6 fold observed in the Pd(II)–promoted reactions Table VII, are very comparable with the rate accelerations of 10^5 to 10^6 fold observed in the base hydrolysis of bidentate glycine ester complexes of copper(II) and cobalt(III) [1, 2]. Intramolecular hydrolyses involving coordinated hydroxide can lead to rate accelerations as high as 10^{11} fold in cobalt(III) systems [2, 14, 15]. In addition, the activation parameters support the view that hydrolysis occurs by hydroxide ion attack on the carbonyl bonded complex as the rate acceleration arises solely due to a more positive value of $\Delta S^{\ddagger}$, with no contribution from the $\Delta H^{\ddagger}$ term. In intramolecular reactions, $\Delta H^{\ddagger}$ factors become of great significance [12].

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