Ester Hydrolysis Catalysed by *ortho*-Palladated Aryl Oximes

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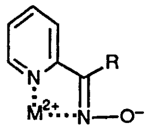
Hydrolysis of 4-nitro- and 2,4-dinitro-phenyl carboxylates proceeds catalytically in the presence of *ortho*-palladated aryl oximes **4**. The catalytic reaction involves two active species, identified as aquated complexes **4** with protonated (k_{AH} path) and deprotonated (k_A path) oximate groups, respectively. Both species contain a weakly basic coordinated hydroxide anion manifested in the k_{AH} path. Other cyclopalladated hydroxo complexes **8**, lacking an oxime group, are shown to react with 2,4-dinitrophenyl acetate with rate constants *ca.* ten times greater than those expected from their basicity. The rate constants k_A obey a Brønsted correlation (β *ca.* 1) with the pK_a of the coordinated oxime group. In neutral solution, palladated oximes react with esters *ca.* 10^3 times faster than the respective free oximes. The *O*-acyl oxime intermediate undergoes very fast hydrolysis through intramolecular attack by the coordinated hydroxide. Factors ensuring the combination of fast acylation and deacylation steps are discussed with reference to some related systems.

The reactivity of coordinated nucleophiles has attracted considerable attention, owing in particular to many similarities between these systems and metalloenzymes.[1–5] Among others, the coordinated oximate group at the *ortho*-position of pyridine **1** has been suggested as a powerful nucleophile for the cleavage of aryl esters[6] and phosphorylimidazole.[7] Further investigation of the system showed the initial reaction product, *i.e.* *O*-acyl oxime, to be hydrolysed in the presence of metal ions.[8–11]

Although this makes the overall reaction catalytic, the system needs high concentrations of metals to be employed (Zn^{2+}, Cu^{2+}, Ni^{2+}) since the *O*-acyl oxime intermediate is a rather poor ligand. Moreover, metals which are more effective in deacylation, *e.g.* Cu^{2+}, so strongly reduce the basicity of the oximate group in the complex **1**, that it completely loses its nucleophilic reactivity.[11]



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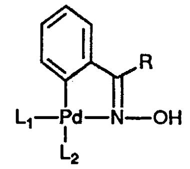

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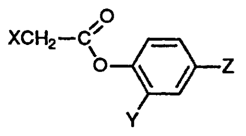
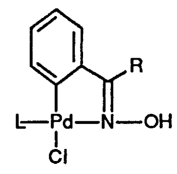


3

a; X = H, Y = Z = NO_2
b; X = Y = H, Z = NO_2
c; X = Y = Z = H
d; X = Cl, Y = H, Z = NO_2
e; X = Cl, Y = Z = NO_2

In a search for a system stable towards dissociation and possessing properly balanced rates of the acylation and deacylation steps, we turned our attention to the structurally related *ortho*-palladated aryl oximes **2** where the metal is covalently bound to the ligand.[12] It was interesting likewise to compare the effect of non-biological and strongly electrophilic 'soft' palladium(II) on the reactivity and basicity of the oximate group with that of previously studied divalent metals. Recently such a comparison was made for the metal-promoted hydrolysis of aminoacid esters.[1,13]

This paper reports the kinetics of hydrolysis of a series of aryl esters **3** catalysed by *ortho*-palladated complexes **4**. The preparation, spectral characteristics and acid–base properties of these complexes were described in previous publications.[14,15]



4

a; R = H, L = pyridine
b; R = Me, L = pyridine
c; R = Et, L = pyridine
d; R = Ph, L = pyridine
e; R = Ph, L = 2,4,6-trimethylpyridine
f; R = Ph, L = methyl 4-pyridinecarboxylate

Experimental

Materials.—*ortho*-Palladated complexes **4a–f**, **9** and **10** were synthesized as described previously.[14] Complexes **8a–e** were prepared as the respective chlorides according to ref. 16. The chloro ligand undergoes fast and quantitative aquation on dissolution of these complexes in water.[16]

Esters **3d, e** were synthesized from the respective phenols and chloroacetyl chloride according to ref. 17. Other esters were commercially available (Fluka) and were purified by recrystallization from ethyl acetate–acetic anhydride (9:1) (**3a**, **b**), or distillation (**3c**).

Kinetic Measurements.—Reaction rates were measured spectrophotometrically using a Hitachi 150-20 UV–VIS spectrophotometer equipped with a thermostatted cell holder.

Kinetic measurements normally used concentrations of esters **3** of *ca.* 1×10^{-4} mol dm^{-3} and concentrations of complexes **4**, **8** and **9** from 1×10^{-5} to 1.5×10^{-4} mol dm^{-3}. The following 0.01 mol dm^{-3} buffer solutions were used at appropriate pH intervals: acetate (3.0–5.5), maleate (5.0–7.0), phosphate (5.5–7.5) and 5,5′-diethylbarbiturate (7.0–9.0). The ionic strength was maintained at 0.1 mol dm^{-3} with $NaClO_4$. The reacting solutions contained 2% (v/v) dimethyl sulfoxide (DMSO) to increase the solubility of the palladium complexes. For the same reason, most of the kinetic experiments were carried out at 45 °C instead of the more commonly used room temperature.

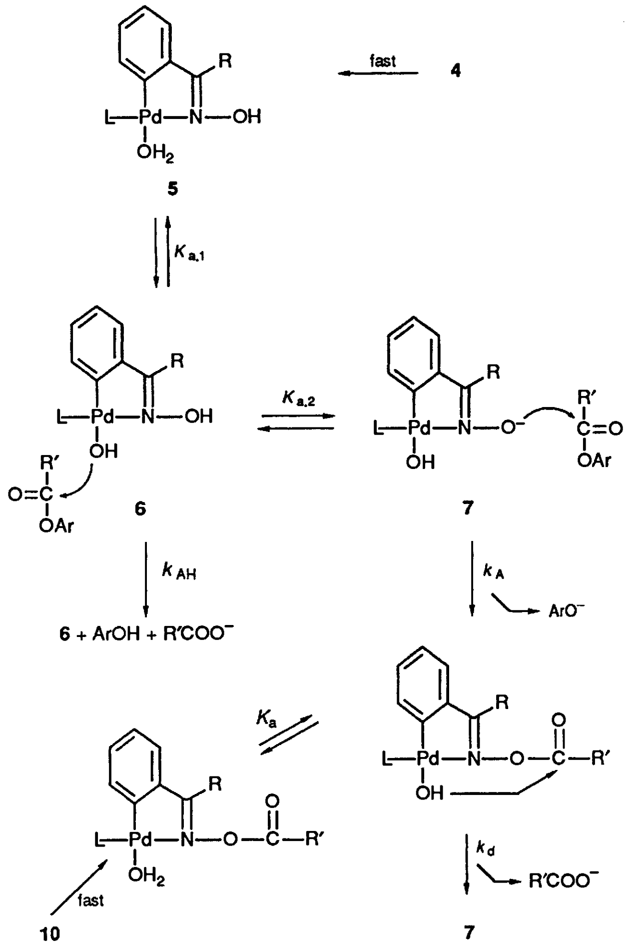
The hydrolysis reactions were monitored by the appearance of the respective phenolate anions or phenols at the wavelengths of their maximum absorbances.

The rate constants were calculated from the initial rates, and in several cases by the integral method.

Kinetics of the deacylation of *ortho*-palladated *O*-acetylbenzophenone oxime **10** was studied in 0.01 mol dm^{-3} acetate buffer solution at 25 °C and ionic strength 0.1 mol dm^{-3}. The reaction was monitored at 280 nm where the difference in absorption of the starting and final complexes was most pronounced. The final spectrum coincided with that of complex **4d** in its aquated form **5**, see Scheme 1. Since the reaction was very fast, the rate constants were calculated by the method of Guggenheim[18] using the recorded part of the kinetic curve obtained after the rapid mixing of prethermostatted solutions of reactants.

Results and Discussion

General Reaction Scheme.—It has been shown previously[15] that complexes **4** undergo fast and irreversible aquation in aqueous solution to form aqua/hydroxo species **5–7** according to Scheme 1 (upper part).



Scheme 1

We have found that the hydrolysis of esters **3**, studied in the pH range 3.5–9, occurs faster in the presence of aquated complexes **4**. As an example, the pseudo-first-order rate constants of the hydrolysis of **3a** are plotted against the concentration of the complex **4d** in Fig. 1. Similar dependences were observed for all other complexes and ester substrates.

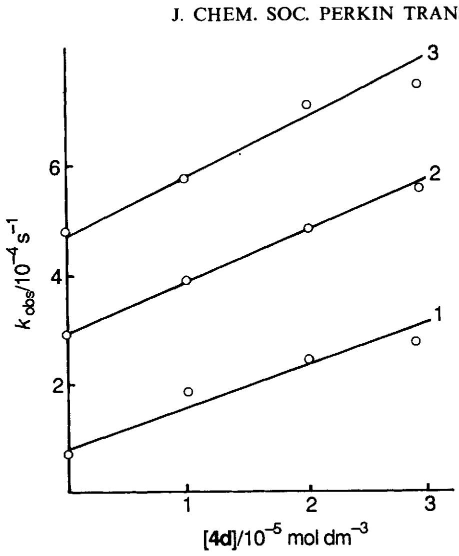


Fig. 1 Observed rate constants of the hydrolysis of **3a** at 45 °C plotted against concentration of the complex **4d** at pH values 7.0, 8.0 and 8.5 (lines 1–3, respectively)

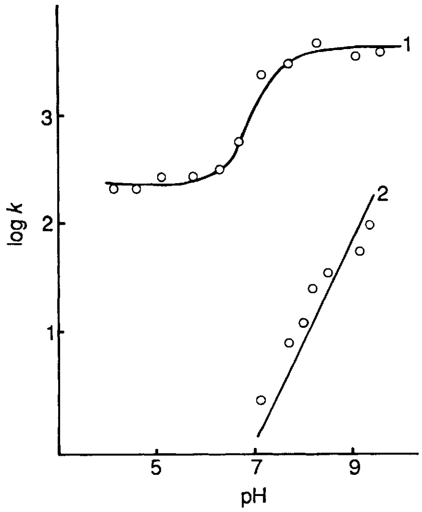


Fig. 2 The pH dependences of logarithms of the observed rate constants of the hydrolysis of **3a** catalysed by the complex **4d** (curve 1) and the oximinolysis of **3a** by free benzophenone oxime (curve 2) at 45 °C

The data in Fig. 1 suggest the rate expression eqn. (1) at a

$$k_{obs} = k_0 + k_{cat}[\text{complex}] \qquad (1)$$

given pH where k_0 refers to the sum of all contributions to hydrolysis (aqueous, base and buffer), which do not involve the complex.

More than ten equivalents of **3a**, with respect to **4d**, were hydrolysed by the complex-dependent path, the rate constant k_{cat} being independent of the reaction progress up to complete ester conversion. This fact demonstrates the catalytic mode of ester hydrolysis by the *ortho*-palladated aryl oximes.

The rate constant k_{cat} derived from the slopes of the lines in Fig. 1 is pH dependent. Its pH dependence, shown in Fig. 2, is characterized by two plateaus separated by an intermediate region with an inflection point near pH 7. This is typical of a mechanism involving two catalytically active species coupled by an acid–base equilibrium. The data were analysed in terms of eqn. (2) where the rate constants k_{AH} and k_A refer to the

$$k_{cat} = \frac{k_{AH}[H^+] + k_A K_a}{[H^+] + K_a} \qquad (2)$$

protonated and deprotonated forms of the catalyst, respectively,

Table 1 Kinetic parameters for the hydrolysis of 2,4-dinitrophenyl acetate, **3a**, by *ortho*-palladated complexes **4** at 45 °C

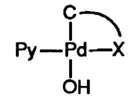
Entry	Complex	k_{AH}/dm^3 mol^{-1} s^{-1}	k_A/dm^3 mol^{-1} s^{-1}	pK_a	pK_{a2}[a]
1	**4a**	3.9	32	6.72	6.89
2	**4b**	26	310	7.14	7.12
3	**4c**	14	300	7.40	7.27
4	**4d**	4.1	79	6.94	7.02
5	**4e**	5.1	24	6.44	
6	**4f**	6.3	94	7.12	
7	**9**		1000		
8	Acetophenone oxime		2300	11.45	
9	Benzophenone oxime		570	11.18	

[a] Found by spectrophotometric titration.[15]

and K_a is the corresponding acidity constant. The numerical values of the rate and equilibrium constants are summarized in Table 1.

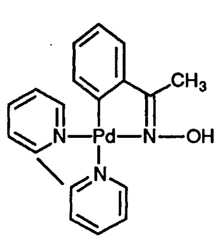
Comparison of pK_{a2} values obtained from the kinetic and spectrophotometric (pK_a in Scheme 1) data for complexes **4** reveals a good coincidence suggesting that both refer to the same process, namely to dissociation of the oxime group. Thus the rate constants k_{AH} and k_A must be attributed to reactions of esters **3** with hydroxo complexes **6** and hydroxo oximato complexes **7**, respectively.

Since oximes react with aryl esters only as the respective oximate anions,[19] the reactivity of complexes **6** is explained by the presence of hydroxide anion as a nucleophilic centre. To confirm the ability of the coordinated hydroxide anion to cleave esters with the required rates, the hydrolysis of esters **3** by cyclopalladated hydroxo complexes **8**, lacking the oxime group, was studied (see below). Dissociation of the oxime group on passing from complexes **6** to **7** generates the oximate nucleophilic centre. The observed increase in the reaction rate may, however, reflect the increased reactivity of the coordinated hydroxide owing to the electron-donating effect of the anionic oximate group. To rule out this explanation, the rate constant for ester hydrolysis by the deprotonated form of the complex **9** lacking a coordinated hydroxide ion was compared with k_A for the complex **4b**, Table 1. Evidently, the reactivity of **9** is even higher than that of **4b**. This means that the coordinated hydroxide does not contribute to the k_A path. The above discussion is summarized in Scheme 1.



8

a; -C X 2-dimethylaminomethylphenyl-1C, N
b; 8-quinolylmethyl-C, N
c; 2-dimethylaminomethylferrocenyl-1C, N
d; 2-(2′-pyridyl) phenyl-1C, N
e; 2-acetylaminophenyl-1C, O



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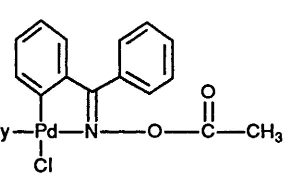

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Reavtivity of the Hydroxo Ligand.—Attempts to demonstrate the deprotonation of coordinated water in complexes **5** by spectrophotometric titration were unsuccessful owing to the negligibly small changes in the absorption induced by dissociation.[15] Therefore, the reactivity of related complexes **8**, the protonation constants of which have been determined previously,[16] towards the ester **3a** was studied. Reaction kinetics followed a simple second-order rate law, first order in each reactant. The second-order rate constants k_{OH}, obtained at pH > pK_a + 1, were independent of pH. They are summarized in Table 2. Evidently, the rate constants k_{OH} are reasonably close to k_{AH}, *cf.* Table 1.

It is of interest to compare k_{OH} with the respective rate constants, found for other metal hydroxo complexes such as $[Co(NH_3)_5OH]^{2+}$, $[Cu(NTA)OH]^{2-}$ *etc.*[20] In Fig. 3, the published data are presented as the solid line (line 2) in Brønsted coordinates according to ref. 20 together with the data from Table 2. Taking into account a 20 °C temperature difference, one can conclude that complexes **8** are *ca.* ten times more reactive than would be expected from their basicity. The reason for this deviation is not clear at the moment. One explanation is that the square planar structure of palladium complexes **8** allows the ester carbonyl to interact with the metal through the axial position in the transition state of the reaction with coordinated hydroxide.

The k_{AH} path was observed only for the most activated esters **3a**, **e**, and was absent with **3b** as the substrate. This is indicative of a rather low reactivity of the hydroxo centre in complexes **6** and **7** compared to that of the oximate group, manifested in the k_A path.

Reactivity of the Oximate Ligand.—Fig. 2 allows us to compare the reactivity of free and complexed oxime ligands (curves 1 and 2). Evidently complex **4d** reacts much faster than benzophenone oxime, the highest difference in the observed rate constants being *ca.* 10^3-fold in neutral solution. Since both palladated and free oximes react with esters **3** in their deprotonated forms, this accelerating effect is completely explicable by the lowering of the pK_a of the oxime group induced by palladium(II), while the coordinated oximate ion is less reactive than the free one (compare lines 4 and 9, as well as 2 and 8 in Table 1).

There are many examples of nucleophilic substitution and addition reactions, including oximinolysis, promoted by metal ions, which act as Lewis acids to enhance the fraction of strongly basic nucleophile in its reactive deprotonated form in neutral aqueous solution.[1–7] Evidently this mechanism can operate

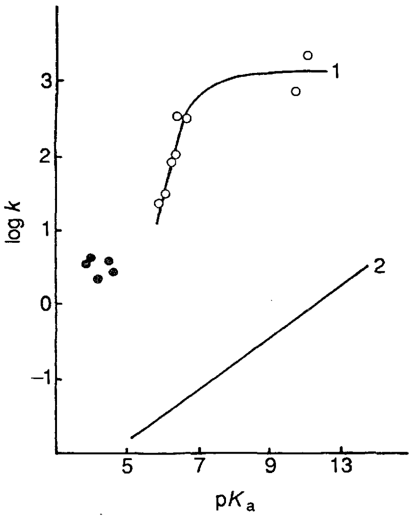

Fig. 3 Brønsted correlations of the data from Table 1 (curve 1) and Table 2 (black circles). The solid line 2 is drawn according to the Brønsted equation given in ref. 20 for the hydrolysis of **3a** by a series of metal aqua complexes.

Table 2 Rate constants for the hydrolysis of 2,4-dinitrophenyl acetate, **3a**, catalysed by complexes **8** at 45 °C

Entry	Complex	pK_a[a]	$k_{OH}/dm^3\ mol^{-1}\ s^{-1}$
1	**8a**	4.18	3.74
2	**8b**	4.91	2.50
3	**8c**	4.14	3.50
4	**8e**	4.46	2.02
5	**8d**	4.84	3.52

[a] Ref. 16.

Table 3 The rate constants for the hydrolysis of esters **3** by complex **4b** (k_A) and oximinolysis of the same esters by acetophenone oximate anion (k_{ox}) at 25 °C

Entry	Ester	$k_A/dm^3\ mol^{-1}\ s^{-1}$	$k_{ox}/dm^3\ mol^{-1}\ s^{-1}$
1	**3a**	50	380
2	**3b**	5.2	42.3
3	**3c**	0.2[a]	—
4	**3d**	2×10^2	9.6×10^3
5	**3e**	2.5×10^3	1.1×10^5

[a] Measured at 45 °C.

only when the lowering of the nucleophile basicity on coordination is not accompanied by a lowering of its reactivity. This implies that both free and coordinated nucleophiles must obey the Brønsted correlation with the coefficient β less than unity, and the most favourable case would be when $\beta = 0$.

The Brønsted correlations for the oximinolysis of the ester **3b** have been thoroughly studied recently.[21,22] It has been shown that they are non-linear[21] and the reactivity of oximate ions levels off when $pK_a > 8$. For more acidic oximes, $\beta = 0.7$ was found.[22] Our results are in accordance with these observations, as illustrated in Fig. 3.

Since pK_a values for all complexes **4** are <8, Table 1, their reactivity follows the Brønsted correlation with a positive coefficient β. The slope of the line drawn through the points for complexes **4** in Fig. 3 is close to unity ($\beta = 1.1 \pm 0.1$; too high a value of β is explicable as an accidental result of the correlation within a very narrow range of acidities of complexes **4**). This means that in this region the expected acceleration due to the metal-induced decrease in pK_a of the oxime group is completely cancelled out by the unfavourable decrease in k_A. On the other hand, the lowering of the pK_a of an oxime, which falls into the levelled region of the Brønsted correlation ($pK_a > 8$), must lead to the proportional acceleration in neutral solution until the pK_a of the oxime group reaches *ca.* 8. So, we can estimate the highest accelerating effect achievable in the systems under discussion as $\leq 10^4$, since typical pK_a values of oximes do not exceed 11–12. Both our present results for complexes **4** and published data for complexes **1** are in agreement with this estimate.

The rate constants k_A for hydrolysis of the whole series of esters **3** were measured with the *ortho*-palladated oxime **4b**. The results are collected in Table 3 together with the rate constants of oximinolysis of the same esters with acetophenone oximate anion (k_{ox}). The same trends in reactivity are observed both for free and coordinated oximate, the ratio k_{ox}/k_A being within 8–50. Phenyl acetate was found to be the least activated ester, which reacts with **4b**, although at an elevated temperature.

The rate constant for the ester **3b** is the most suitable kinetic parameter for comparisons with related systems, since this ester has been widely used as a substrate for the testing of the esterolytic reactivity. The observed k_A is close to the rate constants for oximinolysis of **3b** with oximate ions of comparable basicity, *e.g.* $k_A = 2.4$ and 11.6 dm^3 mol^{-1} s^{-1}, respectively for $Me_2SCH_2COCHNO^-$ ($pK_a = 6.54$) and $MeSO_2CH_2COCHNO^-$ ($pK_a = 7.46$).[22] Complex **1**, where M = Zn and R = H, cleaves **3b** with $k_A = 10$ dm^3 mol^{-1} s^{-1} ($pK_a = 6.5$),[11] which is also comparable to that for **4b**. Complex **1**, where M = Zn and R = Me, possesses an extremely high value of $k_A = 400$ dm^3 mol^{-1} s^{-1} ($pK_a = 7.0$).[11] This rate constant is *ca.* ten times greater than is typical of the most reactive oximate anions with $pK_a > 8$.[21] The reason for this anomaly is not clear. The lack of reactivity of complex **1** with M = Cu[11] is explicable by its low basicity[9] ($pK_a = 3.2$). The rate constant k_A expected on the basis of the Brønsted correlation must be less than 10^{-3} dm^3 mol^{-1} s^{-1}, *i.e.* too small to be measured with typically employed concentrations of reactants. As to complexes **4**, their nucleophilic reactivity towards esters **3** is in accordance with their basicity. The unusual feature of complexes **4** is a very fast decylation of the *O*-acyl oxime intermediate, k_d in Scheme 1.

Deacylation of the O-*Acyl Intermediate.*—Hydrolysis of *O*-acyl oximes proceeds rather slowly.[23] In the particular case of *ortho*-derivatives of pyridine **1**, the reaction is accelerated by divalent metal ions.[8–11] Nevertheless, the rate-determining step of the hydrolysis of the ester **3b** catalysed by the zinc complex **1** is the deacylation step.[11] In the case of complexes **4** both integral kinetics, which were always simple pseudo-first-order and never showed any burst or lag initial periods, and concentration and pH dependences of the initial rates were consistent with a rate-determining acylation step.

The expected *O*-acyl intermediate **10** was prepared in anhydrous conditions and the kinetics of its hydrolysis were studied by spectrophotometry (see Experimental section). The pseudo-first-order deacylation rate constant, $k_{d.obs}$, is plotted against pH in Fig. 4. The observed pH dependence follows the rate eqn. (3) where $k_d = 0.2$ s^{-1} and $pK_a = 5.0$ at 25 °C.

$$k_{d.obs} = \frac{k_d}{1 + [H^+]/K_a} \qquad (3)$$

Comparing k_d with k_A (Table 2) multiplied by the initial concentration of the ester **3** (typically *ca.* 10^{-4} mol dm^{-3}), we obtain for aryl acetates the relationship $k_d \gg k_A[3]$, which means that indeed, the rate-determining step is the acylation of complexes **4**.

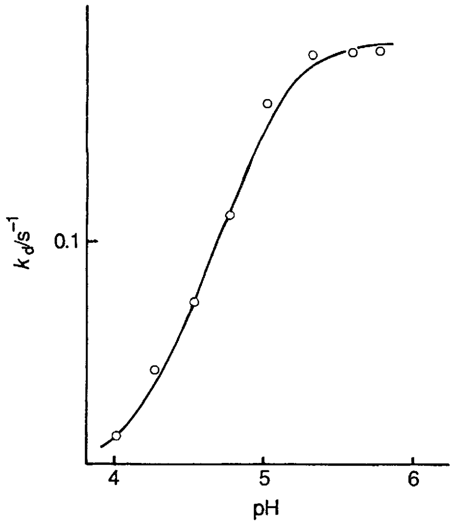

Fig. 4 The pH dependence of the logarithm of observed rate constant of the deacylation of the complex **10** at 25 °C

Eqn. (3) suggests the complex **10** to be involved in the acid–base equilibrium between non-reactive protonated and reactive deprotonated forms. We suppose that, as is typical of other *ortho*-palladated complexes,[16] it loses a chloro ligand immediately on dissolution in water, being converted to a mixture of the respective aqua/hydroxo complexes, Scheme 1 (bottom), *cf.* the behaviour of complexes **4**, Scheme 1 (top). The value of pK_a found from the pH dependence of the rate constant $k_{d.obs}$ is close to those for related complexes **8**, Table 2. The reactive form of the complex **10** is, therefore, its hydroxo form, which undergoes the first-order deacylation.

Hence, the rate constant k_d should be attributed to the intramolecular attack of coordinated hydroxo group at the *O*-acyl function. This conclusion was additionally supported by the observation of the anion inhibition of the deacylation reaction due to the competition of anions and hydroxo ligand [the effect described for the nucleophilic reactions of zinc(II) hydroxo complexes[24]]. The inhibition constants of CH_3COO^- and Cl^- were found to be 30 and 10 $dm^3\ mol^{-1}$, respectively, from kinetic competition experiments.

The intramolecular attack of the coordinated hydroxo group is well documented.[1–3,19,25] This mechanism has also been suggested for the deacylation of zinc(II) and copper(II) *O*-acylated complexes **1**, although the observed pH dependences did not allow the intramolecular rate constants to be calculated.[10] In the case of the most reactive copper(II) complex **1** (R = H),[9] the second-order rate constant for the intermolecular attack of hydroxide anion is $3 \times 10^8\ dm^3\ mol^{-1}$. The respective apparent rate constant for the aqua form of the complex **10** can be calculated from eqn. (3) as $k_dK_a/10^{-14} = 2 \times 10^8\ dm^3\ mol^{-1}$. Thus, in both cases the observed reactivity is very high and approaches the diffusion-controlled limit.

It is noteworthy that the *ortho*-palladated compelxes **4** in their aquated form combine both the high nucleophilic reactivity of complex **1** with M = Zn and the high deacylation rate of the respective complex with M = Cu. The former results from essentially the same basicity of the coordinated oximate group in the zinc complexes **1** and palladium complexes **4** (values of pK_a from 6.5 to 7.5), while the latter is explicable by a complete suppression of the dissociation of the metal from the *O*-acyl intermediate owing to covalent bonding of palladium(II) in complexes **4**. In fact, the expected rate constant for the intramolecular deacylation of the *O*-acylated hydroxo zinc complex **1** evaluated from the published[10] third-order rate constant $k_{OH} = 1.5 \times 10^7\ dm^6\ mol^{-2}\ s^{-1}$, is *ca.* 10 s^{-1} (assuming the pK_a of the zinc-bound water to be the same as in Zn^{2+}_{aq} and the stability constant less than 5 $dm^3\ mol^{-1}$), *i.e.* even more than k_d for the complex **10**.

The behaviour of σ-bonded palladium(II) is quite different from that of simple inorganic forms of palladium(II). We found that complexes **1** (R = H, Me) prepared with $PdCl_4^{2-}$ as the source of the metal did not react with esters **3**, while the respective *O*-acylated oxime underwent fast deacylation in the presence of $PdCl_4^{2-}$ ($k_{d.obs} = 0.05\ s^{-1}$ at pH 5). These observations show the inorganic palladium(II) to be, like copper(II), too electrophilic to give rise to properly balanced rates of the acylation and deacylation steps. The use of the organometallic derivative of palladium(II) provides a solution of the problem, since the σ-aryl group strongly decreases the positive charge on the palladium(II) ion, making the metal-induced shift of the pK_a of the oxime group relatively small, and prevents the dissociation of the metal from the *O*-acyl intermediate enhancing the efficiency of the deacylation step.

Conclusion

Two major principles are realized in catalysis of ester hydrolysis by complexes **4**: generation of nucleophilic oximate and hydroxide ions in neutral solution due to the metal-induced decrease in the pK_a of the oxime group and water, and intramolecular nucleophilic attack of coordinated hydroxide at the acyl group. Both principles operate in hydrolytic metalloenzymes,[2,4] and in this sense, complexes **4** can be considered as biomimetic catalysts, although they contain a non-biological metal.

Complexes **4** are almost perfect esterolytic catalysts among those based on the oximate nucleophile. In fact, as follows from the Brønsted correlations, the highest acylation rate in neutral solution should be observed for oximes with pK_a *ca.* 8, and, on the other hand, the highest deacylation rate would be the diffusion-controlled attack of hydroxide ion on the *O*-acyl intermediate. Evidently, complexes **4** nearly meet these requirements.

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