

Equilibria, Kinetics and Mechanism for Complex Formation Between Hydrogen Sulfate/Sulfate and Palladium(II). Hydrolysis of Tetraaquapalladium(II)

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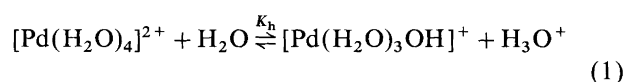
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Spectrophotometric equilibrium measurements indicate formation of the complexes $[\text{Pd}(\text{H}_2\text{O})_3\text{HSO}_4]^+$ and $[\text{Pd}(\text{H}_2\text{O})_3\text{SO}_4]$ in the reaction between $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ and hydrogen sulfate/sulfate in the region: $0.10 \leq [\text{H}^+] \leq 0.80$ M. The stability constants are 0.7 ± 0.2 and $19 \pm 6 \text{ M}^{-1}$, respectively, at 25°C and 1.00 M ionic strength. The protolysis constant for coordinated hydrogen sulfate, i.e. the equilibrium constant for the reaction $[\text{Pd}(\text{H}_2\text{O})_3\text{HSO}_4]^+ + \text{H}_2\text{O} \rightleftharpoons [\text{Pd}(\text{H}_2\text{O})_3\text{SO}_4] + \text{H}_3\text{O}^+$, is 2.5 ± 1.0 M. The stability constant for $[\text{Pd}(\text{H}_2\text{O})_3\text{HSO}_4]^+$ and the protolysis constant for coordinated HSO_4^- are also derived from kinetic measurements as $0.6 \pm 0.2 \text{ M}^{-1}$ and 2.3 ± 1.3 M, respectively. The kinetics for the reversible complex formation reaction, studied by use of stopped-flow spectrophotometry, is first order with respect to palladium complex and total concentration of sulfate, $[\text{S}(\text{VI})]$, with an observed pseudo-first-order rate constant $k_{\text{obsd}} = k_f[\text{S}(\text{VI})] + k_r$ for excess sulfate. Here k_f and k_r denote observed forward second-order and reverse first-order rate constants, respectively. The kinetic data are interpreted in terms of a reaction mechanism which involves parallel and reversible reactions between $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ and HSO_4^- and SO_4^{2-} , respectively, and between $[\text{Pd}(\text{H}_2\text{O})_3\text{OH}]^+$ and HSO_4^- . Forward and reverse rate constants for complex formation between $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ and HSO_4^- are $119 \pm 6 \text{ M}^{-1} \text{ s}^{-1}$ and $210 \pm 60 \text{ s}^{-1}$ at 25°C , indicating that HSO_4^- has a similar nucleophilicity as other oxygen-donor ligands. The rate constants for the reactions of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ with SO_4^{2-} and of $[\text{Pd}(\text{H}_2\text{O})_3\text{OH}]^+$ with HSO_4^- cannot be resolved because of a proton ambiguity. The mononuclear protolysis constant of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ is $\text{p}K_h = 3.0 \pm 0.1$ at 25°C and 1.00 M ionic strength as determined from rapid spectrophotometric equilibrium measurements.

Preparation of tetraaquapalladium(II) perchlorate has been described and various preparative methods discussed.¹ Some of these^{2–7} give rise to formation of polynuclear hydrolysis products or even colloidal species.^{1,7} Solutions of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ with $[\text{HClO}_4] > 0.50$ M are stable without disturbing polynuclear hydrolysis,¹ whereas sluggish and irreversible spectral changes due to formation of polynuclear species can be observed in the timescale of hours in solutions with $[\text{H}^+] < 0.01$ M.^{8–11} A few investigations of the hydrolysis of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$, including equilibrium (1), by use of pH-titrations,⁸ spectrophotometry,⁸ solubility⁹ and kinetic measurements,¹⁰ have appeared. However, the results of these studies are discordant, with values of the protolysis constant K_h ranging from 7.5×10^{-3} to 0.1 M.^{8–10} In the equilibrium studies, the palladium solutions were usually aged for

several hours in order to get observed values constant with time. In this timescale, however, formation of polynuclear complexes is extensive, and this will influence the determination of K_h . Bugarcic¹¹ showed by means of potentiometric titrations that when palladium solutions are aged for a sufficiently long time in the pH region $1.5 < \text{pH} < 3.0$, di- and tetranuclear complexes are formed, whereas the concentration of the monomeric complex $[\text{Pd}(\text{H}_2\text{O})_3\text{OH}]^+$ is negligibly small. Thus, most of the K_h values reported in the literature^{8–10} are not reliable. One purpose of the present work was to determine a more accurate value of K_h , which can be used to rationalise the kinetic data for complex formation between palladium(II) and weakly coordinated protolytic ligands.



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Complex formation between the platinum(II) complex $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ and some simple anions, including sulfate, has been observed by use of ^{195}Pt NMR spectroscopy.¹² For $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$, quantitative information about the stabilities of the weak complexes formed with sulfate is not available.^{13,14} Nor are there any data for kinetics of formation and aequation of palladium(II) sulfato complexes, in spite of the fact that palladium(II) sulfate has occasionally been used as a starting material for kinetic studies.^{10,15}

Experimental

Chemicals and solutions. Stock solutions of tetraaquapalladium(II) perchlorate (ca. 50 mM) in 1.00 M perchloric acid were prepared from palladium sponge (Johnson and Matthey, Specpure) as described previously.¹ The concentrations were determined spectrophotometrically from the absorbance at 380 nm ($\epsilon^{380} = 82.8 \text{ M}^{-1} \text{ cm}^{-1}$).¹ Stock solutions of 1.000 and 2.000 M perchloric acid were prepared from concentrated perchloric acid (Merck, p.a.). Stock solutions of 1.000 M sodium perchlorate were prepared from $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (Merck, p.a.). Anhydrous sodium sulfate (Fluka-Garantie, p.a., >99.5%) was used without further purification. The ionic strength was adjusted to 1.00 M with 1.000 M perchloric acid and sodium perchlorate. Water was doubly distilled from quartz.

Apparatus. Spectra were recorded by use of a Milton Roy 3000 diode array spectrophotometer and thermostatted 1.00 cm quartz Suprasil cells. The kinetics was followed at $25.0 \pm 0.1^\circ\text{C}$ by use of an Applied Photophysics Bio Sequential SX-17 MX stopped-flow ASVD spectrofluorimeter, and rate constants were evaluated by the Applied Photophysics software.¹⁶ Non-linear least-squares curve fittings of experimental data were performed with the KaleidaGraph program for Macintosh.

Hydrolysis of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$. To avoid disturbance from polynuclear complex formation, spectra of a series palladium solutions were recorded as follows: Solutions of 1.000 M HClO_4 and NaClO_4 and a ca. 25 mM stock solution of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ in 1.00 M HClO_4 were thermostatted at 25°C . Palladium solutions with $1.0 \times 10^{-3} \text{ M} \leq [\text{H}^+] \leq 0.04 \text{ M}$ were prepared by rapid dilution of the stock solution of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ with the HClO_4 and NaClO_4 solutions. A small volume of the palladium solution was rapidly injected into a calculated volume of ionic (Na,H) ClO_4 medium by means of a Wheaton micropipette, and the spectrum in the region 200–400 nm was recorded immediately, using a corresponding solution without palladium as a reference. By use of the diode-array instrument, this manipulation required less than 2 min. Formation of polynuclear complexes is insignificant in this short interval of time for the low total concentrations of palladium used. Absorbance values

were read between 210 and 230 nm. Palladium concentrations after dilution varied between 2.465×10^{-5} and $4.93 \times 10^{-4} \text{ M}$.

Spectrophotometric equilibrium measurements. The equilibrium constant for the protolysis of hydrogen sulfate in water, $\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + \text{H}_3\text{O}^+$, has a value of $\text{p}K_a = 1.10 \pm 0.08$ at 25°C and ionic strength 1.00 M.¹⁷ The total concentrations of sulfate are denoted by $[\text{S(VI)}] = [\text{HSO}_4^-] + [\text{SO}_4^{2-}]$. Spectra of solutions with 2.60 mM $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ and with $0.10 \text{ M} \leq [\text{H}^+] \leq 0.80 \text{ M}$ and $0.025 \text{ M} \leq [\text{S(VI)}] \leq 0.200 \text{ M}$, equilibrated for ca. 30 min at 25°C were recorded. A corresponding solution without palladium was used as a reference. Polynuclear hydrolysis of palladium is negligible in the presence of sulfate in this pH region during the time of the experiments. Absorbance values were read at 250 nm.

Stopped-flow measurements. Reaction between $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ and hydrogen sulfate/sulfate was monitored as an increase of absorbance at 250 nm due to complex formation. $[\text{S(VI)}]$ was always kept in a large excess compared to palladium. Kinetic traces could be described by a single exponential. The observed pseudo-first-order rate constants, k_{obsd} , are given as average values from five to seven independent runs. Complex formation was studied as a function of excess $[\text{S(VI)}]$ and $[\text{H}^+]$ using $0.98 \text{ M} \leq C_{\text{Pd}} \leq 4.93 \text{ mM}$, $0.016 \text{ M} \leq [\text{S(VI)}] \leq 0.50 \text{ M}$, and $0.10 \text{ M} \leq [\text{H}^+] \leq 0.70 \text{ M}$. For experiments in the region $0.10 \text{ M} \leq [\text{H}^+] \leq 0.50 \text{ M}$ only freshly prepared palladium solutions were used, in order to avoid disturbance from slow polynuclear complex formation. Values of k_{obsd} as a function of $[\text{S(VI)}]$ and $[\text{H}^+]$ are summarized in Table 1.

Results and discussion

Hydrolysis of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$. Assuming that the second protolysis step can be neglected for $[\text{H}^+] \geq 1.0 \text{ mM}$, the total concentration of palladium, C_{Pd} , can be written as $C_{\text{Pd}} = [\text{Pd}(\text{H}_2\text{O})_4]^{2+} + [\text{Pd}(\text{H}_2\text{O})_3\text{OH}]^+$. The measured absorbances, A_{obsd} , as a function of C_{Pd} and $[\text{H}^+]$ can be derived as eqn. (2), where l denotes the path length

$$A_{\text{obsd}}/C_{\text{Pd}} = (\epsilon_{\text{Pd}} l [\text{H}^+] + \epsilon_{\text{PdOH}} l K_h) / ([\text{H}^+] + K_h) \quad (2)$$

and ϵ_{Pd} and ϵ_{PdOH} the molar absorptivities of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{Pd}(\text{H}_2\text{O})_3\text{OH}]^+$, respectively. The molar absorptivities of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ at different wavelengths were determined by measuring the absorbances of three palladium solutions with $[\text{H}^+] = 1.00 \text{ M}$, where hydrolysis can be neglected. Equation (2) was used to fit the experimental data by a non-linear least-squares method with ϵ_{PdOH} and K_h as adjustable parameters. Figure 1 shows the fitting at 210 nm; fittings at 220 and 230 nm are similar. Calculated values of ϵ_{PdOH} and K_h together with measured ϵ_{Pd} are given in Table 2. The K_h -values are independent of wavelength, and the agreement between them is satisfactory, giving an average value of

Table 1. Observed pseudo-first-order rate constants for the reaction between $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ and $\text{HSO}_4^-/\text{SO}_4^{2-}$ at 25 °C and ionic strength 1.0 M.^a

$[\text{H}^+]/\text{M}$	$[\text{S(VI)}]/\text{M}$	$k_{\text{obsd}}/\text{s}^{-1}$	$k_f/(\text{M}^{-1} \text{s}^{-1})$	k_r/s^{-1}		
0.10	0.010	89 ± 2	438 ± 19	86 ± 1		
0.10	0.020	95 ± 1				
0.10	0.025	96 ± 1				
0.10	0.0375	105 ± 2				
0.10	0.050	107 ± 1				
0.10	0.075	119 ± 1				
0.10	0.100	129 ± 1				
0.20	0.020	98 ± 2			321 ± 4	92 ± 1
0.20	0.025	100 ± 1				
0.20	0.050	109 ± 1				
0.20	0.100	125 ± 1				
0.20	0.150	139 ± 1				
0.20	0.200	156 ± 1				
0.20	0.250	173 ± 2				
0.35	0.025	103 ± 2	257 ± 8	98 ± 1		
0.35	0.050	112 ± 2				
0.35	0.100	125 ± 1				
0.35	0.150	137 ± 1				
0.35	0.200	151 ± 1				
0.35	0.250	161 ± 2				
0.50	0.025	108 ± 2			211 ± 6	104 ± 1
0.50	0.050	116 ± 2				
0.50	0.100	125 ± 2				
0.50	0.150	137 ± 2				
0.50	0.200	147 ± 2				
0.50	0.250	156 ± 2				
0.70	0.025	117 ± 4	194 ± 4	112 ± 1		
0.70	0.050	122 ± 2				
0.70	0.100	132 ± 2				
0.70	0.125	137 ± 2				
0.70	0.150	141 ± 2				

^a $C_{\text{Pd}} = (0.98\text{--}1.9) \times 10^{-3}$ M. The reaction was monitored at 250 nm. The values of k_f and k_r were derived from plots of k_{obsd} vs. $[\text{S(VI)}]$.

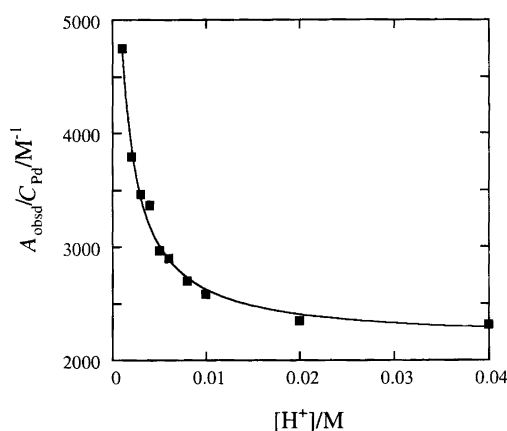


Fig. 1. $A_{\text{obsd}}/C_{\text{Pd}}$ as a function of $[\text{H}^+]$ at 210 nm, 25 °C and ionic strength 1.00 M. C_{Pd} was varied between 2.465×10^{-5} and 4.93×10^{-4} M. The solid line represents the best fit of eqn. (2) to the experimental data.

Table 2. Molar absorptivities and hydrolysis constant at 25 °C and ionic strength 1.00 M.

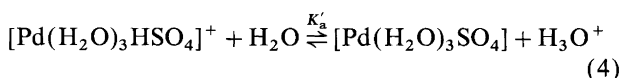
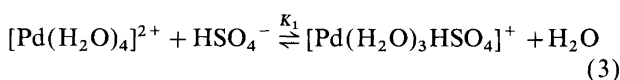
λ/nm	$\epsilon_{\text{Pd}}/\text{M}^{-1} \text{cm}^{-1}$	$\epsilon_{\text{PdOH}}/\text{M}^{-1} \text{cm}^{-1}$	$10^4 K_h/\text{M}$
210	2165	$(7.3 \pm 0.5) \times 10^3$	10.0 ± 1.4
220	698	$(4.9 \pm 0.4) \times 10^3$	9.9 ± 1.4
230	167	$(2.2 \pm 0.2) \times 10^3$	9.7 ± 1.6
		Average	9.9 ± 1.4

$K_h = (9.9 \pm 1.4) \times 10^{-4}$ M or $\text{p}K_h = 3.0 \pm 0.1$. Absorbance changes as a function of $[\text{H}^+]$ at wavelengths > 230 nm are too small to allow an accurate evaluation of K_h and ϵ_{PdOH} .

The present experiments were designed to circumvent polynuclear complex formation, affording a more accurate (and much smaller) value of K_h than those reported in previous studies, ranging between 7.5×10^{-3} and 0.10 M.⁸⁻¹⁰ Hydrolysis of the analogous platinum complex $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ has been studied qualitatively, and its $\text{p}K_h$ -value has been estimated to be > 2.5 .¹⁸ This is in good agreement with the present result, since tetraaquapalladium(II) and -platinum(II) are expected to have similar $\text{p}K_h$ -values due to their similar charge and bond distances.

Recently, $[\text{Pd}(\text{H}_2\text{O})_3\text{OH}]^+$ has been used as a promotor for selective hydrolysis of peptides.¹⁹⁻²¹ In these studies, the palladium(II) perchlorate solutions with pH 1.0 were supposed to contain mainly $[\text{Pd}(\text{H}_2\text{O})_3\text{OH}]^+$ based on the literature value^{8,9} of $K_h = 0.1$ M. The present results indicate that such solutions only contain ca. 1 mol% of the monohydroxo complex, as long as polynuclear complex formation can be neglected.

Sulfate complex formation equilibria. Complex formation between tetraaquapalladium(II) and sulfate in strongly acidic solutions has been observed qualitatively.^{13,14} The equilibrium constant for reaction (3) has been reported to be $0.30 \pm 0.01 \text{ M}^{-1}$ at 25 °C as determined by spectrophotometry.¹⁴ In the present pH region $0.10 \text{ M} \leq [\text{H}^+] \leq 0.80 \text{ M}$, the mol% of HSO_4^- varies from 91 to 56% and that of SO_4^{2-} from 9 to 44%, respectively. It follows that the complex $[\text{Pd}(\text{H}_2\text{O})_3\text{HSO}_4]^+$ as well as $[\text{Pd}(\text{H}_2\text{O})_3\text{SO}_4]$ has to be taken into account in the equilibrium data treatment. The equilibria involved can be expressed as eqns. (3) and (4), if only 1 : 1 complexes are assumed to be formed under the experimental conditions used.



The measured absorbances of equilibrated solutions, A_{obsd} , as functions of C_{Pd} and of $[\text{S(VI)}]$, are expressed as eqn. (5) by introducing $K_h/[\text{H}^+] \leq 0.01$ in the present

pH region. Here A_0 denotes the absorbance at $[S(VI)] = 0$ and at various acidities, ε_1 and ε_2 are the molar absorptivities of $[Pd(H_2O)_3HSO_4]^+$ and $[Pd(H_2O)_3SO_4]$, respectively, and the total concentration of palladium is

$$C_{Pd} = [Pd(H_2O)_4^{2+}] + [Pd(H_2O)_3OH^+] + [Pd(H_2O)_3HSO_4^+] + [Pd(H_2O)_3SO_4].$$

As before, l denotes path length.

$$A_{obsd} = \frac{A_0 + m_1 l C_{Pd} [S(VI)]}{1 + m_2 [S(VI)]} \quad (5)$$

Here, the parameters m_1 and m_2 are defined as

$$m_1 = (\varepsilon_1 K_1 [H^+] + \varepsilon_2 K_1 K'_a) / (K_a + [H^+]) \quad (6)$$

$$m_2 = (K_1 [H^+] + K_1 K'_a) / (K_a + [H^+]) \quad (7)$$

Equation (5) was used to analyse the measured absorbances as a function of $[S(VI)]$ at different acidities by a non-linear least-squares routine with m_1 and m_2 as adjustable parameters. The fits are shown in Fig. 2, giving the values of m_1 and m_2 listed in Table 3. The good fits also imply that the assumption of formation of only 1:1 complexes is reasonable. This is further supported by the fact that the kinetic experiments give no indication of formation of higher complexes, since all kinetic traces are well described by single exponentials.

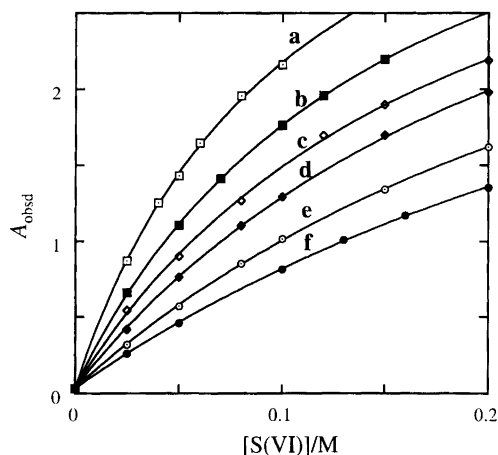


Fig. 2. Observed absorbances at 250 nm, A_{obsd} , as a function of $[S(VI)]$ at 25 °C and ionic strength 1.00 M. The solid lines represent the best fit of eqn. (5) to the experimental data. $[H^+] = 0.10$ (a), 0.20 (b), 0.30 (c), 0.40 (d), 0.60 (e) and 0.80 M (f).

Table 3. Values of the parameters m_1 and m_2 of eqns. (5)–(7) evaluated at 250 nm and 25 °C from the plots in Fig. 2.

$[H^+]/M$	m_1/M^{-2}	m_2/M^{-1}
0.10	$(1.61 \pm 0.03) \times 10^4$	9.4 ± 0.5
0.20	$(1.12 \pm 0.01) \times 10^4$	6.7 ± 0.1
0.30	$(8.7 \pm 0.2) \times 10^3$	5.3 ± 0.2
0.40	$(6.9 \pm 0.1) \times 10^3$	4.0 ± 0.2
0.60	$(4.90 \pm 0.05) \times 10^3$	2.9 ± 0.1
0.80	$(3.78 \pm 0.05) \times 10^3$	2.3 ± 0.1

Equation (7) was fitted to the values of m_2 as a function of $[H^+]$ by use of the literature value of $K'_a = 0.079 M$.¹⁷ The fit is shown in Fig. 3a, affording $K_1 = 0.7 \pm 0.2 M^{-1}$ and $K'_a = 2.5 \pm 1.0 M$, respectively. After substitution of these values into eqn. (6), m_1 as a function of $[H^+]$ was accordingly fitted and is shown in Fig. 3b. Subsequently, the values of $\varepsilon_1 = (1.4 \pm 0.4) \times 10^3$ and $\varepsilon_2 = (1.6 \pm 0.4) \times 10^3 M^{-1} cm^{-1}$ at 250 nm were derived.

Kinetics. Plots of the observed rate constants in Table 1 vs. excess $[S(VI)]$ at different acidities are linear with non-zero intercepts, corresponding to the rate expression of eqn. (8), where k_f and k_r denote the observed forward second-order and reverse first-order rate constants, respectively. Values of k_f and k_r as a function of $[H^+]$ calculated from the experimental data are given in Table 1 also.

$$k_{obsd} = k_f [S(VI)] + k_r \quad (8)$$

Reaction mechanism. By taking into account the protolytic equilibria of both the metal ion and hydrogen sulfate, the reaction mechanism can be described as in Scheme 1, involving eqns. (9)–(12).

According to this mechanism and by use of $K_h \ll [H^+]$ and $K'_h \ll [H^+]$, expressions for k_f and k_r in eqn. (8) are derived as eqns. (13) and (14).

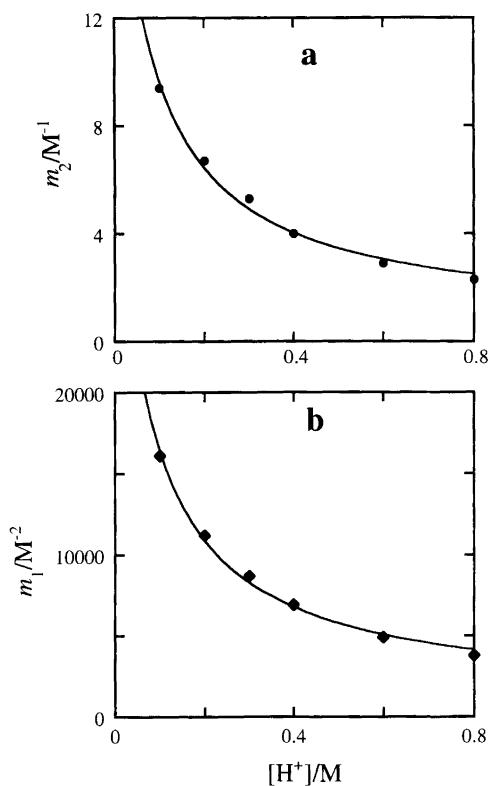


Fig. 3. (a) Plot of m_2 as a function of $[H^+]$ according to eqn. (7). (b) Plot of m_1 vs. $[H^+]$ according to eqn. (6). Solid lines represent the best fit of the equations to the data.

observed for carboxylic acids,²²⁻²⁵ O-bonded dimethyl sulfoxide²⁹ and for water exchange at palladium(II).³⁰ Thus, as expected, all these oxygen-bonded nucleophiles show a similar reactivity towards the palladium(II) center.

There is a proton ambiguity involved in the reaction mechanism of Scheme 1. The pathways described by eqns. (10) and (11) in Scheme 1 have a similar proton concentration dependence, i.e. the terms of $(k_2K_a + k_3K_h)$ and $(k_{-2} + k_{-3})$ in eqns. (13) and (14), respectively. From the values of the two terms, two limiting cases can be examined. (i) If $k_3 = k_{-3} = 0$, $k_2 = 830 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-2} = 81 \text{ s}^{-1}$. The rate constant of $830 \text{ M}^{-1} \text{ s}^{-1}$ seems reasonable, since substitution at $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ takes place by an associative mechanism.^{22-24,29-31} Alternatively, if $k_2 = k_{-2} = 0$, then $k_3 = 6.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-3} = 81 \text{ s}^{-1}$. There are so far no kinetic data for $[\text{Pd}(\text{H}_2\text{O})_3\text{OH}]^+$ reactions available for comparison, in contrast to the well known fact that $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ is about three orders of magnitude more reactive than $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.³² At least, reaction of $[\text{Pd}(\text{H}_2\text{O})_3\text{OH}]^+$ with HSO_4^- could not *a priori* be excluded at present. In this regard, more kinetic data for reactions of square-planar hydroxo complexes are needed.

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