

163. Water-Exchange Mechanism of Tetraaquapalladium(II). A Variable-Pressure and Variable-Temperature Oxygen-17 NMR Study¹⁾

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Summary

Water exchange of square-planar $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ has been studied as a function of temperature (240 to 345 K) and pressure (0.1 to 260 MPa, at 324 K) by measuring the ^{17}O -FT-NMR line-widths of the resonance from coordinated water at 27.11 and 48.78 MHz. The following exchange parameters were obtained: $k_{\text{ex}}^{298} = (560 \pm 40) \text{ s}^{-1}$, $\Delta H^* = (49.5 \pm 1.9) \text{ kJ mol}^{-1}$, $\Delta S^* = -(26 \pm 6) \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta V^* = -(2.2 \pm 0.2) \text{ cm}^3 \text{ mol}^{-1}$. The values refer to an aqueous perchlorate medium with an ionic strength between 2.0 and 2.6 *m* and a perchloric-acid concentration between 0.8 and 1.7 *m*, and are interpreted in terms of an associative (a) activation for the exchange. The exchange rate for $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ is 1.4×10^6 times faster than for $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ at 298 K. A comparison with reactions between other nucleophiles and $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ is also made.

Introduction. – Ligand-substitution reactions of four-coordinate square-planar complexes, especially those of Pt, have been extensively investigated. On the other hand, only very few studies of solvent-exchange kinetics of such complexes have been reported [2–4]. However, exchange reactions between solvated cations and bulk solvent are more fundamental than ordinary substitution reactions in many respects. Parameters such as entropies and volumes of activation are more easily interpreted for reactions which do not involve any net chemical change. For octahedrally coordinated metal ions, the experimental information on solvent exchange rates and activation parameters is now becoming relatively complete [5].

The main reason for the present lack of information on solvent-exchange kinetics of square-planar metal ions is the fact that square-planar solvato species are not very common or easy to handle in the high concentrations often required to study solvent-exchange kinetics by NMR.

The only two solvent-exchange reactions of square-planar complexes studied so far, seem to be the slow water exchange of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$, which has been followed both by the use of ^{195}Pt -NMR [2] and ^{17}O -NMR spectroscopy at various temperatures and pressures [4], and the much faster dimethyl-sulfide exchange of *trans*- $\text{Pd}(\text{Me}_2\text{S})_2\text{Cl}_2$ in vari-

¹⁾ Part 23 of the series 'High-Pressure NMR Kinetics'. For part 22, see [1].

ous organic diluents, which was followed as a function of temperature and pressure by the use of $^1\text{H-NMR}$ [3]. We here report an investigation of the water exchange of $\text{Pd}(\text{H}_2\text{O})_4^{2+}$. This reaction is sufficiently fast to be followed by the $^{17}\text{O-NMR}$ line-broadening technique.

Experimental. – 1. *Chemicals and Solutions.* Stock solutions of $\text{Pd}(\text{ClO}_4)_2$ were prepared by dissolving ca. 4.5 g Pd sponge (*Johnson and Matthey*, spectrographically standardized) in several portions of hot fuming HNO_3 (100%, *Merck, p.a.*, total volume ca. 300 ml) in a 400 ml beaker. The solution was boiled cautiously for ca. 2 h to reduce its volume to ca. 150 ml. It was transferred to an evaporation dish and the HNO_3 was removed by repeated evaporations (Caution!) with several 50 ml portions of conc. HClO_4 (*Baker, p.a.*, 70–72%, total volume used ca. 250 ml). Further details are given elsewhere [6]. The final volume of the solution was ca. 80 ml, the Pd concentration 0.495M (calculated spectrophotometrically from the absorbance at 380 nm, where the molar absorptivity of $\text{Pd}_{\text{aq}}^{2+}$ is $82.8 \text{ cm}^{-1} \text{ M}^{-1}$ [6]) and the HClO_4 concentration 12M. The absorption spectrum of a diluted sample of this solution agreed with previously reported spectra for $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ [6]. Low absorbances in the wavelength region 250 to 300 nm indicated that polynuclear hydrolysis was negligible [6].

The composition of the five solutions used for the NMR experiments are summarized in *Table 1*. They were prepared by mixing weighed quantities of Pd-stock solutions and ^{17}O -enriched water (*Yeda, Israel*, ca. 40 atom-%, normalized in ^1H). To solutions 3 and 4, solid NaHCO_3 (*Merck, p.a.*) was added cautiously under stirring to decrease the HClO_4 concentration to half of its initial value. Measurements were also performed with and without paramagnetic Mn(II) which was added to the solutions as the solid perchlorate $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (*Merck, p.a.*). After mixing, all solutions contained 37 atom-% ^{17}O .

Table 1. *Composition of Solutions* (molal units). All solutions contained 37 atom-% ^{17}O .

| Solutions | $[\text{Pd}(\text{ClO}_4)_2]/m$ | $[\text{HClO}_4]/m$ | $[\text{NaClO}_4]/m$ | $[\text{Mn}(\text{ClO}_4)_2]/m$ | Ionic Strength/ m |
|-------------------|---------------------------------|---------------------|----------------------|---------------------------------|---------------------|
| 1 ^{a)} | 0.070 | 1.67 | 0 | 0.23 | 2.57 |
| 2 ^{a)b)} | 0.073 | 1.74 | 0 | 0 | 1.96 |
| 3 ^{a)c)} | 0.067 | 0.81 | 0.81 | 0.23 | 2.51 |
| 4 ^{a)b)} | 0.073 | 0.88 | 0.86 | 0 | 1.96 |
| 5 ^{c)} | 0.069 | 1.67 | 0 | 0.24 | 2.60 |

^{a)} Variable-temperature experiments at 27.11 MHz.

^{b)} Variable-temperature experiments at 48.78 MHz.

^{c)} Variable-pressure experiments at 27.11 MHz.

2. *Instrumentation.* The $^{17}\text{O-NMR}$ spectra were recorded by use of a *Bruker CXP-200* spectrometer equipped with a 4.7 T wide-bore cryomagnet working at 27.11 MHz and a *Bruker WH-360* instrument with a 8.4 T magnet working at 48.78 MHz. The temp. of the 10-mm NMR tubes was held constant within $\pm 0.3 \text{ K}$ by use of a *Bruker BVT-1000* unit and was measured by a substitution technique using a Pt resistor [7]. Variable pressure measurements were performed up to 260 MPa at 27.11 MHz by use of a high-pressure probe described in [8]. Absorption spectra were recorded by use of *Cary 14* and *Perkin-Elmer-Hitachi 340* instruments.

3. *NMR Measurements.* Two examples of the spectrometer parameters used to record spectra with line-widths varying from 100 to 3000 Hz are given in the caption of *Fig. 1*.

Two different types of spectra were obtained. Solutions without added paramagnetic Mn(II) display two resonances separated by 131.8 ppm (*Fig. 1*). The high-intensity one is due to bulk water and the smaller one to water molecules coordinated to Pd(II) . At higher temperatures, when the water exchange between the palladium ion and free water becomes faster, the latter signal broadens. It becomes impossible even by use of the high-field spectrometer (8.4 T) to separate it from the resonance of the free water molecules, which is ca. 200 times bigger.

Solutions which contain $\text{Mn}(\text{ClO}_4)_2$, on the other hand, only display the resonance from water coordinated to Pd(II) . The large bulk water signal is suppressed, Mn(II) acting as a very efficient relaxation agent for this signal because of its long electron relaxation time and its very fast coordinated/bulk water-exchange rate. For example, at 298 K the bulk water line-width of a 0.23 *m* Mn(II) solution is about 80 kHz [9]. It has been checked up to 333 K that the addition of Mn(II) had no effect on the observed relaxation rates (see *Fig. 2*).

The transverse relaxation rate, $1/T_{2b}$, from water coordinated to Pd(II) was obtained from the line-width at half height, $\Delta\nu_{1/2}$, of its NMR signal fitted to a *Lorentzian* curve, and using the relation $1/T_{2b}^{\text{H}} = \pi\Delta\nu_{1/2}$.

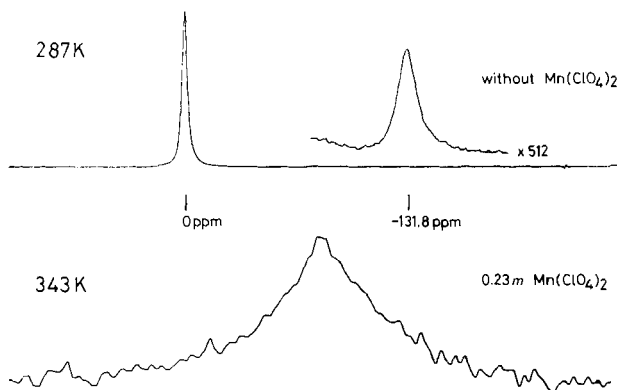


Fig. 1. 27.11-MHz ^{17}O -NMR spectra of 0.07 *m* $[\text{Pd}(\text{H}_2\text{O})_4](\text{ClO}_4)_2$ and 1.7 *m* HClO_4 solutions in 37% enriched water, with and without added $\text{Mn}(\text{ClO}_4)_2$. The upper (lower) spectrum is the result of 7200 (100 000) scans using a repetition rate of 100 (20) msec and a pulse width of 15 (10) μsec (90° pulse = 50 μsec) in the quadratic detection mode; 4 (2) K data points were used over a total spectral width of 20 000 (83 000) Hz and an exponential filter of 10 (40) Hz was used. Same abscissa for both spectra.

Results and Data Treatment. – In the limit of slow exchange, the Pd(II) bound water relaxation rate is given by Eqn. 1, where T_{20}^b is the quadrupolar relaxation time

$$1/T_2^b = 1/T_{20}^b + 1/\tau \quad (1)$$

and τ the mean life-time of water in the first coordination sphere. From transition state theory the temperature dependence of τ and its relation to the pseudo-first-order rate constant, k_{ex} , for the exchange of a particular water molecule [10] has the form shown in Eqn. 2.

$$k_{\text{ex}} = 1/\tau = \frac{(k_B \cdot T)}{h} \exp(\Delta S^*/R - \Delta H^*/RT) \quad (2)$$

The volume of activation, ΔV^* , is defined according to transition state theory as in Eqn. 3, and the pressure dependence of the rate constant can be expressed by Eqn. 4, where k_0 is the rate constant at zero pressure.

$$\Delta V^* = -RT(\partial \ln k / \partial P)_T \quad (3)$$

$$\ln k_p = \ln k_0 - \Delta V^* P / RT \quad (4)$$

The quadrupolar relaxation rate was assumed to obey an Arrhenius temperature dependence according to Eqn. 5, where $1/T_{20}^{b298}$ is the contribution at 298.15 K and E_Q is the corresponding activation energy.

$$1/T_{20}^b = 1/T_{20}^{b298} \exp \left[\frac{E_Q}{R} (1/T - 1/298.15) \right] \quad (5)$$

Tables 2 and 3 summarize the $1/T_{20}^b$ data. Fig. 2 shows the temperature dependence for high (1.64 and 1.74 *m*) and low (0.81 and 0.88 *m*) concentrations of HClO_4 , respectively, and in the absence and presence of Mn(II). The exchange and NMR parameters

Table 2. Relaxation Rates, $1/T_2^b$, of the Bound Water ^{17}O -NMR Signal of $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ at Ambient Pressure and Different Temperatures in 37% Enriched ^{17}O Water

| $\approx 1.7\text{ m HClO}_4$ | | | | $\approx 0.8\text{ m HClO}_4$ | | | |
|-------------------------------|-------------------------|--------------------------|-------------------------|-------------------------------|-------------------------|--------------------------|-------------------------|
| Solution 1 ^{a)} | | Solution 2 ^{b)} | | Solution 3 ^{a)} | | Solution 4 ^{b)} | |
| T/K | $1/T_2^b/\text{s}^{-1}$ | T/K | $1/T_2^b/\text{s}^{-1}$ | T/K | $1/T_2^b/\text{s}^{-1}$ | T/K | $1/T_2^b/\text{s}^{-1}$ |
| 239.5 | 6877 ^{c)} | 255.4 | 2760 ^{c)} | 242.6 | 3737 ^{c)} | 255.4 | 2734 ^{c)} |
| 243.7 | 5167 | 261.7 | 1818 | 243.7 | 3637 | 261.7 | 1915 |
| 249.6 | 3944 | 268.1 | 1501 | 245.4 | 3501 | 268.1 | 1569 |
| 257.1 | 2543 | 274.6 | 1260 | 257.1 | 1927 | 274.6 | 1293 |
| 263.7 | 1916 | 280.7 | 1091 | 264.5 | 1651 | 280.7 | 1213 |
| 272.5 | 1353 | 286.6 | 1045 | 278.2 | 1077 | 286.6 | 1152 |
| 278.2 | 1193 | 293.7 | 1042 | 290.0 | 965 | 293.7 | 1045 |
| 281.6 | 1162 | 300.4 | 1193 | 305.8 | 1099 | 300.4 | 1153 |
| 295.7 | 1021 | 307.7 | 1680 | 311.4 | 1383 | 307.7 | 1518 |
| 305.8 | 1318 | 314.4 | 1984 | 319.7 | 2167 | 314.4 | 1874 |
| 313.8 | 1884 | | | 323.9 | 3252 | | |
| 319.7 | 2186 | 312.4 | 2061 ^{d)} | 333.1 | 4226 | 312.4 | 2057 ^{d)} |
| 323.6 | 3405 | 317.4 | 2716 | 339.4 | 6575 | 317.4 | 2768 |
| 335.5 | 6601 | 324.0 | 3222 | 341.4 | 9395 | 324.0 | 3431 |
| 341.4 | 9256 | 328.7 | 4470 | 344.7 | 9720 | 328.7 | 4207 |
| | | 332.8 | 5185 | | | 332.8 | 5194 |

a) With 0.23 m Mn^{2+} . b) Without Mn^{2+} . c) At 27.11 MHz. d) At 48.78 MHz.

Table 3. Relaxation Rates, $1/T_2^b$, of the Bound Water ^{17}O -NMR Signal of $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ at Different Pressures in 37% Enriched ^{17}O Water

| 1.67 m HClO_4 ^{a)} | | 0.81 m HClO_4 ^{b)} | |
|--------------------------------------|-------------------------|--------------------------------------|-------------------------|
| P/MPa | $1/T_2^b/\text{s}^{-1}$ | P/MPa | $1/T_2^b/\text{s}^{-1}$ |
| 0.1 | 3715 ^{c)} | 4.0 | 2919 ^{c)} |
| 50 | 3858 | 50 | 2896 |
| 100 | 4101 | 100 | 3041 |
| 150 | 4443 | 150 | 3143 |
| 200 | 4460 | 200 | 3093 |
| 230 | 4624 | 260 | 3334 |
| 182.5 | 4333 | 222 | 3334 |
| 170 | 4474 | 175 | 3143 |
| 125 | 4273 | 125 | 3023 |
| 75 | 3980 | 75 | 2896 |
| 25 | 3889 | 25 | 2836 |
| 0.1 | 3756 | 2.5 | 2774 |

a) Solution 5 at 325.3 K. b) Solution 3 at 323.2 K. c) At 27.11 MHz.

contained in Table 4 result from least squares fitting of these data to Eqn. 1, 2 and 5, with ΔH^* , ΔS^* , $1/T_{20}^{\text{b}298}$ and E_0^{b} as adjustable parameters. Calculations by use of the high- and low-acidity values separately gave no significant differences for the kinetic parameters between these two series of measurements. As expected, the small change of ionic strength for the various solutions, or the addition of $\text{Mn}(\text{II})$ was also of no importance on the exchange rate constants. However, at temperatures below ca. 290 K differences were observed between the quadrupolar relaxation rates for the high-

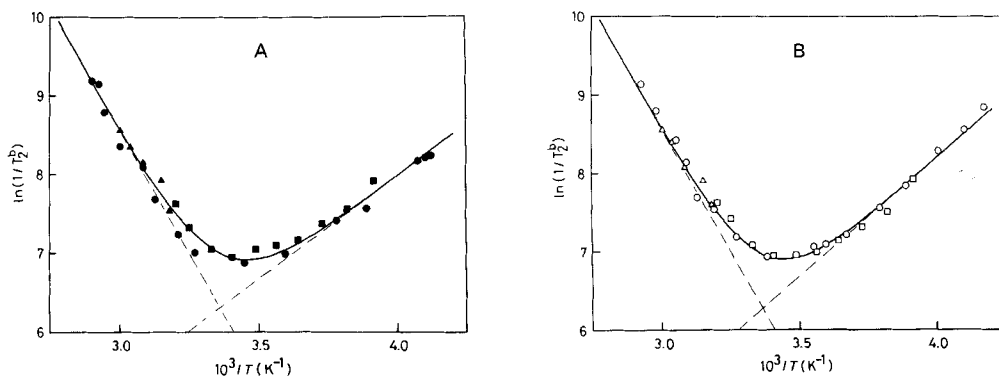


Fig. 2. Temperature dependence of the relaxation rates, $1/T_2^b$, of the bound-water ^{17}O -NMR signal of various $\text{Pd}(\text{ClO}_4)_2$ solutions with various pH, in the absence and presence of $\text{Mn}(\text{II})$. (A) Solutions 3 (●) and 4 (■, ▲) with low acidity (0.81 and 0.88 m HClO_4) with (●) and without (■, ▲) Mn^{2+} . (B) Solutions 1 (○) and 2 (□, △) with high acidity (1.7 m HClO_4) with (○) and without (□, △) Mn^{2+} . Measurements performed at 27.11 MHz (○, □, ●, ■) and 48.78 MHz (△, ▲). Concentrations are given in Table 1.

Table 4. Kinetic and NMR Parameters for $\text{Pd}(\text{H}_2\text{O})_4^{2+}$. Errors represent one standard deviation.

| Variable temperature: | | | | |
|--|-----------------------|-----------------------|-----------------|-----------------|
| Set of data ^{a)} | 1 and 2 ^{b)} | 3 and 4 ^{c)} | 1 to 4 | |
| $10^{-2}k_{\text{ex}}^{298}/\text{s}^{-1}$ | 6.3 ± 0.5 | 4.7 ± 0.6 | 5.6 ± 0.4 | |
| $10^{-3}k_{\text{ex}}^{323}/\text{s}^{-1}$ | 3.07 ± 0.08 | 2.63 ± 0.12 | 2.87 ± 0.07 | |
| $\Delta H^*/\text{kJmol}^{-1}$ | 48.2 ± 2.1 | 52.3 ± 3.1 | 49.5 ± 1.9 | |
| $\Delta S^*/\text{JK}^{-1}\text{mol}^{-1}$ | -30 ± 6 | -18 ± 9 | -26 ± 6 | |
| $1/T_{20}^{b298}/\text{s}^{-1}$ | 465 ± 33 | 613 ± 59 | $510 \pm 38^f)$ | $543 \pm 43^g)$ |
| E_Q^b | 26.7 ± 1.1 | 19.9 ± 1.5 | 25.3 ± 1.3 | 21.6 ± 1.3 |
| Variable pressure: | | | | |
| Set of data ^{a)} | 5 ^{b)} d) | 3 ^{c)} e) | 5 and 3 | |
| $\Delta V^*/\text{cm}^3\text{mol}^{-1}$ | -2.6 ± 0.2 | -1.7 ± 0.1 | -2.2 ± 0.2 | |
| $10^{-3}k_{\text{ex,ol}}/\text{s}^{-1}$ | 3.56 ± 0.03 | 2.81 ± 0.03 | 3.59 ± 0.03 | 2.79 ± 0.03 |

^{a)} Composition of the solutions are given in Table 1. ^{b)} High acidity. ^{c)} Low acidity. ^{d)} At 325.3 K. ^{e)} At 323.2 K. ^{f)} Set 1 and 2. ^{g)} Set 3 and 4.

and low-acidity solutions. Therefore, the final set of parameters of Table 4 was obtained by use of all variable temperature data in one calculation with six adjustable parameters: ΔH^* , ΔS^* (or k_{ex}), and high- and low-acidity $1/T_{20}^b$ and E_Q^b .

The temperature of ca. 324 K chosen for the two variable pressure experiments results from a compromise between a lower temperature for better signal to noise ratio and a higher temperature to minimize the $1/T_{20}^b$ contribution to $1/T_2^b$. At 324 K, the quadrupolar contribution to the observed relaxation rate was less than 10%, and could, therefore, be considered as pressure independent in the variable pressure data analysis. The rate constants obtained by difference (Eqn. 1) were first analyzed separately for the high- and low-acidity data set with ΔV^* and k_0 as adjustable parameters (Eqn. 4). The good agreement between the results from both data sets (Table 4) leads us to a final analysis of all variable pressure data with three adjustable parameters: ΔV^* , and high- and low-acidity set k_0 . This analysis is shown in Fig. 3.

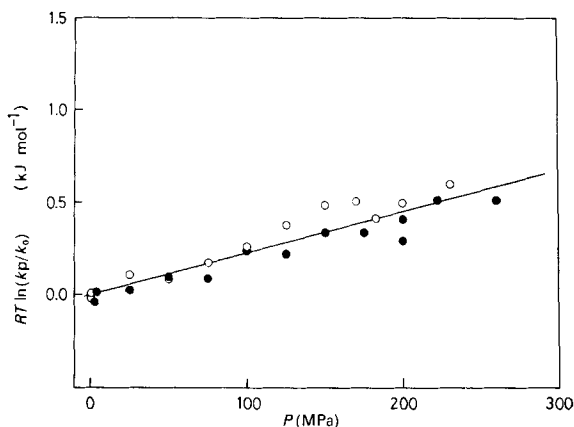


Fig. 3. Pressure dependence of the water exchange of $\text{Pd}(\text{H}_2\text{O})_4^{2+}$. (○) Solution 5 at 325.3 K, and (●) solution 3 at 323.2 K and 27.11 MHz. Concentrations in Table 1.

Discussion. – The only two square-planar hydrated cations known so far are those of Pd(II) and Pt(II). At ambient temperature, they both display an ^{17}O -NMR signal upfield from bulk water, at -131.8 ppm for the former (Fig. 1) and at -124.3 ppm for the latter [4]. The kinetic parameters displayed in Table 5 indicate that the Pd-complex exchanges its aqua ligands 1.4×10^6 times faster than that of Pt. This is in excellent agreement with previously observed reactivity differences between Pd and Pt aquahalide complexes [11] [12].

Table 5. Kinetic Parameters for Water Exchange of Square-planar Hydrated Cations

| | $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ | $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ |
|---|--|--|
| $k_{\text{ex}}^{298}/\text{s}^{-1\text{a}}$ | $(5.6 \pm 0.4) \times 10^2$ | $(3.9 \pm 0.3) \times 10^{-4}$ |
| $\Delta H^*/\text{kJmol}^{-1}$ | 49.5 ± 1.9 | 89.7 ± 2.4 |
| $\Delta S^*/\text{JK}^{-1}\text{mol}^{-1}$ | -26 ± 6 | -9 ± 8 |
| $\Delta V^*/\text{cm}^3\text{mol}^{-1}$ | $-2.2 \pm 0.2^{\text{b}}$ | $-4.6 \pm 0.2^{\text{c}}$ |
| Ref. | This paper | 4 |

^{a)} For the exchange of a particular water molecule of $\text{M}(\text{H}_2\text{O})_4^{2+}$. ^{b)} At 324 K. ^{c)} At 297 K.

The negative values of ΔS^* and the slightly negative ΔV^* are compatible with an associative activation mode for the water exchange. Since these are the only known activation parameters for solvent exchange on square-planar tetrasolvates great care should be taken in the detailed interpretation of the results, until more data have been recorded. At this stage it might even not be possible to definitively exclude a limiting associative (A) mechanism, despite the small ΔV^* values.

Other kinetic data, however, indicate that an associative interchange (I_a) mechanism is very likely for substitution reaction of Pd-complexes. The substitution rates depend strongly on the nature of the entering ligand, but there is also a leaving-ligand effect. Both bond-making and bond-breaking are, therefore, probably significant in the formation of the transition state. Tables 6 and 7 contain kinetic parameters for some substitution reactions, related to the present water exchange.

Table 6. Rate Constants and Activation Parameters at 25° for Reaction 6 between $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and Various Entering Ligands X

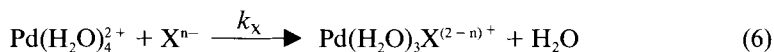
| X | $k_X^{298}/\text{M}^{-1}\text{s}^{-1}$ | $k_X/k_{\text{H}_2\text{O}}$ | $\Delta H^*/\text{kJ mol}^{-1}$ | $\Delta S^*/\text{JK}^{-1}\text{mol}^{-1}$ | $\Delta V^*/\text{cm}^3\text{mol}^{-1}$ | Ref. |
|----------------------------|--|------------------------------|---------------------------------|--|---|------------|
| $(\text{CH}_3)_2\text{SO}$ | 2.6 | 0.06 | 58 | -44 | -10.4 | [13] [14] |
| H_2O | 41 ^{a)} | 1 | 50 | -48 ^{a)} | -2.2 | This paper |
| CH_3CN | 130 | 3 | 43 | -61 | - | [13] |
| Cl^- | 1.83×10^4 | 4×10^2 | 42 | -25 | - | [12] |
| Br^- | 9.2×10^4 | 2×10^3 | 42 | -13 | - | [12] |
| I^- | 1.1×10^6 | 3×10^4 | 12 | -75 | - | [15] |

^{a)} Rate constant and ΔS^* for exchange of one of the four-coordinated water molecules recalculated to second-order units, i.e. $4 k_{\text{ex}}^{298}/55$.

Table 7. Rate Constants and Activation Parameters at 25° for Acid Hydrolysis of Various Complexes $\text{PdX}(\text{H}_2\text{O})_3^{(2-n)+}$, where X is the Leaving Ligand, Reaction 7. Data from references 12, 13 and 15

| Complex | X | k_X^{298}/s^{-1} | $\Delta H^*/\text{kJ mol}^{-1}$ | $\Delta S^*/\text{JK}^{-1}\text{mol}^{-1}$ | $\Delta V^*/\text{cm}^3\text{mol}^{-1}$ | Ref. |
|--|------------------------|---------------------------|---------------------------------|--|---|------------|
| $\text{Pd}(\text{H}_2\text{O})_3\text{Cl}^+$ | Cl^- | 0.8 | 59 | -55 | - | [12] |
| $\text{Pd}(\text{H}_2\text{O})_3\text{Br}^+$ | Br^- | 0.8 | 59 | -55 | - | [12] |
| $\text{Pd}(\text{H}_2\text{O})_3\text{I}^+$ | I^- | 0.8 | 55 | -50 | - | [15] |
| $\text{Pd}(\text{H}_2\text{O})_3\text{CH}_3\text{CN}^{2+}$ | CH_3CN | 24 | 54 | -65 | - | [13] |
| $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ | H_2O | 560 | 50 | -26 | -2.2 | This paper |

In Table 6, data for three neutral and three negatively charged entering ligands in Reaction 6 are given. There is a large entering-ligand-effect, approximately of the same



order of magnitude as for the corresponding Pt(II)-complexes [2]. The increase in relative rate is paralleled by a decrease of ΔH^* , as expected for associative activation. The extremely slow rate of entry of the dimethyl sulfoxide molecule into the coordination sphere of Pd(II) is remarkable. It can probably be attributed to oxygen-bonding of the molecule in the rate-determining step. Sulfur donors (for instance thiocyanate) are usually much more efficient as entering ligands to Pt- and Pd-complexes [16] [17].

The nature of the leaving ligand is also important for the rate of these substitution reactions, although this effect is smaller. This is illustrated by Table 7, which contains kinetic parameters for Reaction 7.



Thus, the present results on water exchange on $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ are, in keeping with other kinetic data for substitution reactions of Pd(II)-complexes, indicative of an associative mode of activation for this reaction.

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