

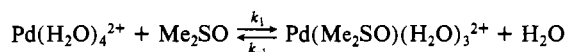
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Kinetics and Thermodynamics for Complex Formation between Palladium(II) and Dimethyl Sulfoxide as a Function of Temperature and Pressure¹

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The kinetics and equilibrium for complex formation between Pd(H₂O)₄²⁺ and dimethyl sulfoxide have been studied as a function of temperature (277–311 K) and pressure (1–200 MPa). Two complexes, Pd(Me₂SO)(H₂O)₃²⁺ and Pd(Me₂SO)₂(H₂O)₂²⁺, are formed for Me₂SO concentrations <0.8 M. Spectrophotometric equilibrium measurements at ambient pressure give stepwise stability constants $K_1^{298} = 9.0 \pm 0.6 \text{ M}^{-1}$ and $K_2^{298} = 0.4 \pm 0.2 \text{ M}^{-1}$ and ¹H NMR measurements give $K_1^{298} = 7.0 \pm 0.2 \text{ M}^{-1}$ and $K_2^{298} = 0.3 \pm 0.2 \text{ M}^{-1}$. The temperature dependence of K_1 studied by ¹H NMR gives $\Delta H^\circ_1 = -7.3 \pm 0.3 \text{ kJ mol}^{-1}$ and $\Delta S^\circ_1 = -8.4 \pm 1.2 \text{ J K}^{-1} \text{ mol}^{-1}$. The pressure dependence of K_1 studied spectrophotometrically gives $\Delta V^\circ_1 = -7.5 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ at 298 K. Stopped-flow spectrophotometry at ambient pressure gives $k_1^{298} = 2.45 \pm 0.04 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-1}^{298} = 0.24 \pm 0.01 \text{ s}^{-1}$, $\Delta H^\ddagger_1 = 58 \pm 1 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger_{-1} = 69 \pm 1 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger_1 = -44 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta S^\ddagger_{-1} = -25 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$ for the process



NMR line broadening gives the rate constant for formation of Pd(Me₂SO)₂(H₂O)₂²⁺ from Pd(Me₂SO)(H₂O)₃²⁺ as $k_2^{298} = 100 \pm 50 \text{ M}^{-1} \text{ s}^{-1}$. High-pressure stopped-flow experiments at 298 K give $\Delta V^\ddagger_1 = -9.2 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$ and $\Delta V^\ddagger_{-1} = -1.7 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$, which together with the value of ΔV°_1 define the volume profile for the formation of the first complex. All values refer to 1.00 M ionic strength. The negative values of the entropies and volumes of activation are consistent with an associative mode of activation. The Me₂SO molecule is an inefficient entering ligand. The mechanism for complex formation is discussed. It might involve a rate-determining attack via the oxygen atom of the Me₂SO molecule, followed by rapid isomerization to the thermodynamically more stable S-bonded form.

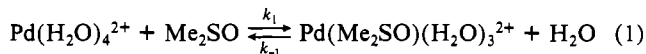
Introduction

There is a still growing interest in the use of high-pressure techniques in kinetic studies.³ For solvent-exchange and complex-formation reactions, the main effort over the last years in this field has been on the elucidation of substitution mechanisms of octahedrally coordinated transition-metal cations by use of volumes of activation.⁴ The number of studies involving square-planar complexes is in contrast very small, although their kinetics at ambient pressure have been extensively studied.⁵ For simple exchange or complex-formation reactions involving square-planar metal centers, on the other hand, the information so far is limited to water exchange on Pt(H₂O)₄²⁺^{6,7} and Pd(H₂O)₄²⁺⁸ and to dimethyl sulfide exchange on *trans*-Pd(Me₂S)₂Cl₂.⁹

The aim of the present work is to study a simple complex-formation reaction on Pd(H₂O)₄²⁺ with an uncharged monodentate ligand. Mechanistic conclusions from such simple systems are expected to be more clear-cut than those involving charged or multidentate ligands.¹⁰ Previous kinetic studies on complex-formation reactions with Pd(H₂O)₄²⁺ involve halide ligands at ambient pressure only,^{11–13} and high-pressure studies so far have been restricted to studies of steric hindrance in substitution reactions of a series of square-planar diethylenetriamine and sub-

stituted diethylenetriamine complexes of palladium(II).^{14,15}

Dimethyl sulfoxide, Me₂SO, forms strong complexes with platinum(II),^{16,17} and it has often been used as a trans-labilizing ligand in reactions with platinum(II) complexes.^{17–19} The trans effect of Me₂SO coordinated to palladium is not known. Me₂SO appeared to be a suitable entering ligand for this first high-pressure investigation of a simple complex-formation reaction of a square-planar aqua ion (eq 1).



Experimental Section

Chemicals and Solutions. Stock solutions of Pd(ClO₄)₂ (ca. 50 mM) in 1.00 M aqueous HClO₄ (Baker p.A.) were prepared from palladium sponge (Johnson and Matthey, Spec. pure) as described previously.²⁰ Dimethyl sulfoxide, Me₂SO (BDH, Spectralgrade, and Fluka, p.A.), was freshly distilled under reduced pressure at 343 K over calcium hydride, and stock solutions were prepared by mixing with aqueous perchloric acid to give an acid concentration of 1.00 M. Protolysis of Pd(H₂O)₄²⁺ and formation of Me₂SOH⁺ are negligible under those experimental conditions.^{20,21} All solutions had a constant ionic strength of 1.00 M fixed with perchloric acid.

Spectrophotometric Equilibrium Measurements. Absorption spectra were recorded at 298.2 K by use of a Cary 14 double-beam spectrophotometer equipped with thermostated cells. Figure 1 shows spectral changes due to complex formation. Spectrophotometric equilibrium measurements were performed at 258 and 365 nm with the Cary instrument and with a Zeiss PMQ II spectrophotometer. The total concentrations of palladium varied between 9×10^{-5} and $4.5 \times 10^{-3} \text{ M}$ and those of Me₂SO between 0 and 0.8 M. The absorbance of Me₂SO is negligible at 365 nm and for most experiments at 258 nm also ($\epsilon^{258} = 0.03 \text{ cm}^{-1} \text{ M}^{-1}$). Blank solutions containing Me₂SO in appropriate concentrations were used. All absorbances were constant for at least 3 days.

The pressure dependence of the stability constant K_1 was measured at 370 nm with a Perkin-Elmer 340 spectrophotometer, equipped with a high-pressure optical cell described elsewhere²² and thermostated at

- (1) A preliminary account of this work can be found in: Ducommun, Y.; Nichols, P. J.; Helm, L.; Elding, L. I.; Merbach, A. E. *J. Phys. C* **1984**, *45*, C8–221. In Figure 7 of this reference, the temperature should read 298 K.
- (2) (a) University of Lausanne. (b) University of Lund. (c) Present address: Inorganic Chemistry, Chalmers University of Technology, S-412 96 Gothenburg, Sweden.
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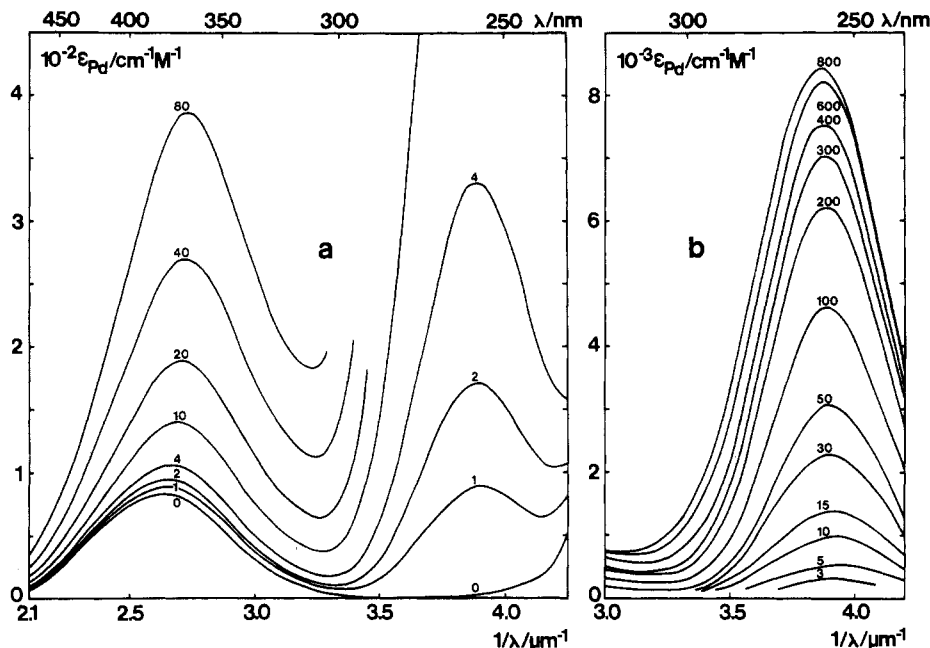


Figure 1. Spectra of equilibrated solutions at 298.2 K. The total concentration of palladium, C_{Pd} /mM, was 4.53 (a) and 8.92×10^{-2} (b). The total concentrations of Me_2SO , $C_{\text{Me}_2\text{SO}}$ /mM, are given in the figure. The bottom spectrum in (a) represents $\text{Pd}(\text{H}_2\text{O})_4^{2+}$.

298.2 K. Measurements were performed up to 200 MPa. The sample had $C_{\text{Pd}} = 1.23$ mM and $C_{\text{Me}_2\text{SO}} = 115$ mM, sufficient to form about 50% of the Me_2SO mono complex (cf. Figure 2).

NMR Measurements. ^1H NMR spectra were recorded on a Bruker AM 400 spectrometer at five temperatures between 272.5 and 311.3 K for a solution with $C_{\text{Pd}} = 19.6$ mM and $C_{\text{Me}_2\text{SO}} = 49.2$ mM and at four temperatures between 277.7 and 294.7 K for a solution with $C_{\text{Pd}} = 19.6$ mM and $C_{\text{Me}_2\text{SO}} = 800$ mM.

Stopped-Flow Measurements. Variable-temperature measurements at ambient pressure were performed at 258 and 365 nm with a Durrum-Gibson stopped-flow instrument operated at 287.9, 298.2, and 308.2 K. Excess palladium or Me_2SO ensured pseudo-first-order kinetics. The concentration of Me_2SO was kept below 0.2 M, where the concentration of the second complex is negligible (cf. Figure 2). Most of the runs with excess palladium were also monitored by use of the Zeiss PMQ II instrument, by mixing equal volumes of the reactants into the cell with thermostated syringes and recording the change of absorbance with time at 365 nm.

The high-pressure stopped-flow instrument used for the variable-pressure work is described elsewhere.^{1,23} Data were collected at 365 nm up to 175 MPa at 298 K, with $C_{\text{Pd}} = 1.0$ mM and a variable excess of Me_2SO (<0.2 M).

Calculations and Results

The stability constants are defined by eq 2, where $n = 1, 2$.

$$K_n = \frac{[\text{Pd}(\text{Me}_2\text{SO})_n(\text{H}_2\text{O})_{4-n}^{2+}]}{([\text{Pd}(\text{Me}_2\text{SO})_{n-1}(\text{H}_2\text{O})_{5-n}^{2+}][\text{Me}_2\text{SO}]} \quad (2)$$

The spectrophotometric equilibrium measurements at ambient pressure were analyzed by means of a nonlinear least-squares minimizing program based on the STEPIT procedure.²⁴ The best fit was obtained when accounting for two complexes, with stepwise stability constants $K_1^{298} = 9.0 \pm 0.6 \text{ M}^{-1}$ and $K_2^{298} = 0.4 \pm 0.2 \text{ M}^{-1}$ and molar absorptivities of $\epsilon_1^{258} = (1.01 \pm 0.06) \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, $\epsilon_1^{365} = 870 \pm 40 \text{ cm}^{-1} \text{ M}^{-1}$, $\epsilon_2^{258} = (9.84 \pm 0.05) \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$, and $\epsilon_2^{365} = 850 \pm 3 \text{ cm}^{-1} \text{ M}^{-1}$ for the Me_2SO mono and bis complexes, respectively. The distribution of palladium between the different species calculated from those stability constants is shown in Figure 2.

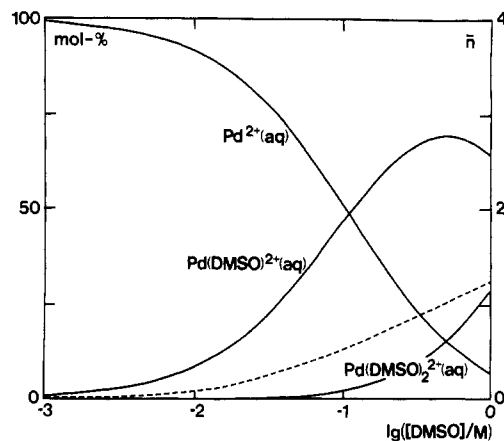


Figure 2. Distribution of palladium between the various complexes and the mean ligand number, \bar{n} (dashed line), as a function of $\log([\text{Me}_2\text{SO}]/\text{M})$ at 298 K calculated from $K_1 = 9.0 \text{ M}^{-1}$ and $K_2 = 0.4 \text{ M}^{-1}$ (1.00 M perchloric acid medium).

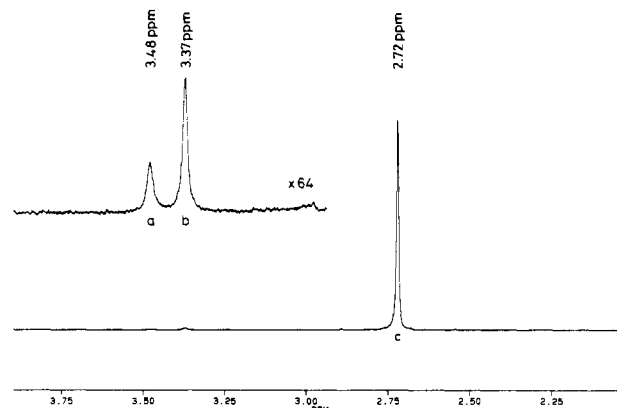


Figure 3. ^1H NMR spectrum of a solution with $C_{\text{Me}_2\text{SO}} = 800$ mM and $C_{\text{Pd}} = 19.6$ mM, showing the chemical shifts of coordinated Me_2SO in the Me_2SO bis complex (a) and in the mono complex (b) and of free Me_2SO (c) as referred to sodium 3-(trimethylsilyl)propanesulfonate.

The NMR spectra of solutions with low Me_2SO concentration display two signals, one from the free Me_2SO and the other from $\text{Pd}(\text{Me}_2\text{SO})(\text{H}_2\text{O})_3^{2+}$ 0.65 ppm downfield. From the relative areas

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Table I. Rate Constants, Activation Parameters, and Thermodynamic Parameters at 298 K^a

	stopped-flow	equilibria UV	NMR	simultaneous fit of all variable-pressure data
$k_1^{298}/\text{M}^{-1}\text{s}^{-1}$	2.45 ± 0.04^b			
$k_{-1}^{298}/\text{s}^{-1}$	0.24 ± 0.01^b			
$k_2^{298}/\text{M}^{-1}\text{s}^{-1}$			100 ± 50	
$\log(K_1^{298}/\text{M}^{-1})$	1.01^c	0.95 ± 0.01	0.85 ± 0.01	
$\log(K_2^{298}/\text{M}^{-1})$		-0.4 ± 0.2	-0.5 ± 0.3^d	
$\Delta H_1^*/\text{kJ mol}^{-1}$	58 ± 1			
$\Delta H_{-1}^*/\text{kJ mol}^{-1}$	69 ± 1			
$\Delta H_1^\circ/\text{kJ mol}^{-1}$	-11^e		-7.3 ± 0.3	
$\Delta S_1^*/\text{J K}^{-1}\text{ mol}^{-1}$	-44 ± 3			
$\Delta S_{-1}^*/\text{J K}^{-1}\text{ mol}^{-1}$	-25 ± 3^f			
$\Delta S_1^\circ/\text{J K}^{-1}\text{ mol}^{-1}$	-19^g		-8.4 ± 1.2	
$\Delta V_1^*/\text{cm}^3\text{ mol}^{-1}$	-10.4 ± 0.5			-9.2 ± 0.6
$\Delta V_{-1}^*/\text{cm}^3\text{ mol}^{-1}$	-0.9 ± 0.2			-1.7 ± 0.6
$\Delta V_1^\circ/\text{cm}^3\text{ mol}^{-1}$		-5.8 ± 0.1		-7.5 ± 0.3

^aIn 1.00 M perchloric acid medium. Errors quoted are standard deviations. ^bExperiments with excess palladium (Figure 4a) give $k_1^{298} = 2.7 \pm 0.3 \text{ M}^{-1}\text{s}^{-1}$ and $k_{-1}^{298} = 0.22 \pm 0.01 \text{ s}^{-1}$. ^cCalculated as k_1/k_{-1} . ^d278 K. ^eCalculated as $\Delta H_1^* - \Delta H_{-1}^*$. ^fCalculated from pseudo-first-order constants. ^gCalculated as $\Delta S_1^* - \Delta S_{-1}^*$.

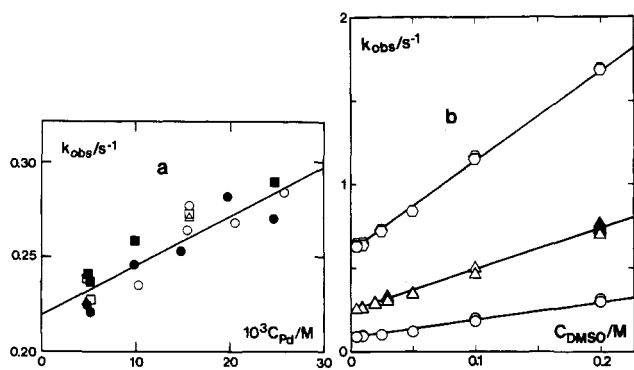


Figure 4. Pseudo-first-order rate constants as a function of excess reactant at ambient pressure: (a) excess palladium at 298.2 K for $C_{\text{Me}_2\text{SO}}/\text{mM} = 0.20$ (Δ), 0.25 (\circ), 0.50 (\square), 2.50 (\bullet), and 5.0 (\blacksquare); (b) excess Me_2SO at 287.9 (\circ), 298.2 (Δ), and 308.2 K (\circ). Open symbols denote stopped-flow experiments and filled ones conventional spectrophotometric data.

of those peaks, the stability constant could be calculated as $K_1^{298} = 7.0 \pm 0.2 \text{ M}^{-1}$. The temperature variation of K_1 gave $\Delta H_1^\circ = -7.3 \pm 0.3 \text{ kJ mol}^{-1}$ and $\Delta S_1^\circ = -8.4 \pm 1.2 \text{ J K}^{-1}\text{ mol}^{-1}$ for reaction 1.

At higher concentrations of Me_2SO , an additional signal 0.76 ppm downfield from the free Me_2SO signal confirms the presence of the Me_2SO bis complex, as shown by Figure 3. The second stepwise stability constant could be obtained at 277.7 K as $K_2^{278} = 0.3 \pm 0.2 \text{ M}^{-1}$. The two peaks are slightly broadened by exchange, and they coalesce into a single peak at higher temperatures. A computer simulation of this exchange process was possible by assuming a three-site exchange. The rate constant for formation of the Me_2SO bis complex from the mono complex could be roughly estimated from those measurements between 277.2 and 311.3 K to be $k_2^{298} = 100 \pm 50 \text{ M}^{-1}\text{s}^{-1}$.

The observed rate constants k_{obsd} from the stopped-flow and conventional kinetic experiments were obtained from a linear least-squares analysis of at least the first 3 half-lives and represent the average of two to six experiments. The rate constants for the forward and reverse reactions in eq 1 were derived by fitting the k_{obsd} values at various excess reagent concentrations [R] to eq 3.

$$k_{\text{obsd}} = k_1 + k_{-1}[\text{R}] \quad (3)$$

Figure 4 shows the concentration dependence of k_{obsd} . The k_1 and k_{-1} values obtained at the three temperatures allow the calculation of the corresponding enthalpies and entropies of activation through a fit to the Eyring equation. Table I contains the values obtained for these parameters. As can be seen in Table I, the agreement between the values of K_1 obtained from direct equilibrium mea-

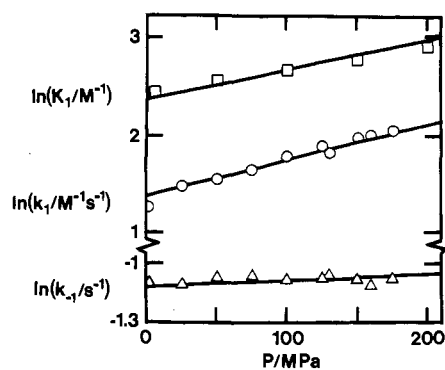


Figure 5. Effect of pressure on the stepwise stability constant and on the rate constants for reaction 1 at 298 K. The lines through the points represent the result of the simultaneous fit of all kinetic and equilibrium data.

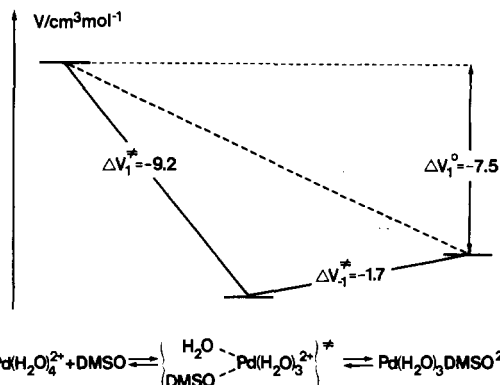


Figure 6. Volume profile for the reaction between $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and Me_2SO in aqueous solution.

surements (UV and NMR) and those calculated as $K_1 = k_1/k_{-1}$ from the kinetic data of Figure 4 is excellent.

Figure 5 shows the pressure dependence of the equilibrium constant and of the rate constants for forward and reverse reactions in a logarithmic scale. Stopped-flow kinetic data as a function of pressure were analyzed by fitting to eq 4 and 5, where k_1° and

$$\ln k_1 = \ln k_1^\circ - \Delta V_1^* P/RT \quad (4)$$

$$\ln k_{-1} = \ln k_{-1}^\circ - \Delta V_{-1}^* P/RT \quad (5)$$

$$\ln K_1 = \ln K_1^\circ - \Delta V_1^\circ P/RT \quad (6)$$

k_{-1}° are also parameters. Equation 6 was used for the spectrophotometric equilibrium data, with K_1° and ΔV_1° as adjustable

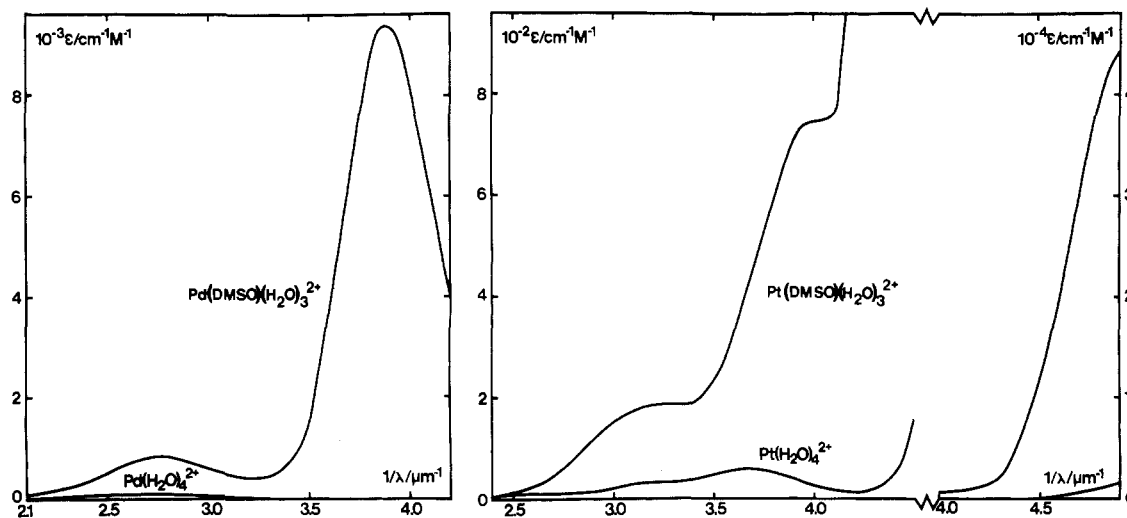


Figure 7. UV spectra of $M(\text{H}_2\text{O})_4^{2+}$ and $M(\text{Me}_2\text{SO})(\text{H}_2\text{O})_3^{2+}$ ($M = \text{Pd}, \text{Pt}$) at 298 K for a 1.00 M perchloric acid medium (ref 35 and calculation from data in ref 17 and in Figure 1).

parameters. The results of those calculations are given in columns 2–4 of Table I.

The kinetic and thermodynamic data were also simultaneously fitted to eq 4–6, yielding the values of ΔV^\ddagger_1 , ΔV^\ddagger_{-1} , and ΔV^\ddagger_{-1} contained in column 5 of Table I. Those values define the volume profile of reaction 1 shown in Figure 6.

Discussion

With a stability constant of $K_1 \approx 8 \text{ M}^{-1}$, $\text{Pd}(\text{Me}_2\text{SO})(\text{H}_2\text{O})_3^{2+}$ is at least 10^6 times weaker than its platinum analogue with $K_1 > 10^7 \text{ M}^{-1}$.¹⁷ S-bonding ligands like thiocyanate or thiourea, for instance, normally form very stable complexes with both palladium and platinum, although the palladium analogues are usually somewhat weaker. In $\text{Pt}(\text{Me}_2\text{SO})(\text{H}_2\text{O})_3^{2+}$ Me_2SO coordinates to platinum via the sulfur atom.¹⁷ The big difference in stability observed in the present case could be due to oxygen bonding of the Me_2SO molecule in aqueous solutions of palladium(II) or to an equilibrium between S- and O-bonded isomers. This would be contrary to the situation in the solid state, where crystal structure determinations have shown that complexes of both palladium and platinum containing one or two Me_2SO molecules coordinate those via sulfur.^{25–29} In addition, recent EXAFS studies have shown that, in solution, both $\text{Pd}(\text{Me}_2\text{SO})_4^{2+}$ and $\text{Pt}(\text{Me}_2\text{SO})_4^{2+}$ contain two S-bonded ligands in positions cis to each other,³⁰ which is the case in the solid state also.^{27,31} The close similarity between the UV spectra of $\text{Pd}(\text{Me}_2\text{SO})(\text{H}_2\text{O})_3^{2+}$ and $\text{Pt}(\text{Me}_2\text{SO})(\text{H}_2\text{O})_3^{2+}$ shown in Figure 7 also indicates that dimethyl sulfoxide is bonded in the same way in these two complexes, i.e. via the sulfur. O-bonding would be expected to cause much smaller differences in the d–d and charge-transfer bands than observed, when compared to the case for the spectra of the $M(\text{H}_2\text{O})_4^{2+}$ complexes.

The much lower stability of the palladium complex compared to that of platinum could be rationalized in terms of differences in electronic structure. In the platinum complex, the σ interactions are stronger, and—probably more important—there is a more extensive back-bonding from filled metal d orbitals to empty orbitals of the sulfur with suitable symmetry. Another observation in support of this interpretation is that Pd–S bonds are significantly

Table II. Rate Constants for Formation (k_1) and Aquation (k_{-1}) of $\text{PdL}(\text{H}_2\text{O})_3^{(2-n)+}$ in Aqueous Solution at 298 K^a

L^{n-}	$k_1/\text{M}^{-1} \text{ s}^{-1}$	k_{-1}/s^{-1}	ref
H_2O	41 ^b	560 ^c	8
Me_2SO	2.45	0.24	this work
Cl^-	1.8×10^4	0.83	11
Br^-	9.2×10^4	0.83	11
I^-	1.1×10^6	0.92	13

^a In 1.00 M perchloric acid medium. ^b Water-exchange rate per coordination site, $k_{\text{ex}} = 560 \text{ s}^{-1}$, recalculated to second-order units, $4k_{\text{ex}}/55$. ^c Water-exchange rate k_{ex} for a particular water molecule.

longer than Pt–S bonds in analogous Me_2SO complexes in the solid state.³¹

There also seems to be a difference in kinetic trans effect of Me_2SO when complexes of palladium and platinum are compared. In the case of palladium, the present results indicate that the entry of the second Me_2SO ligand is only about 20–50 times faster than the formation of $\text{Pd}(\text{Me}_2\text{SO})(\text{H}_2\text{O})_3^{2+}$. This might suggest that the trans effect of Me_2SO coordinated to palladium is much smaller (ca. 100–300 relative to H_2O) than its trans effect in platinum complexes, which has been estimated to be ca. 2×10^6 relative to H_2O .¹⁷

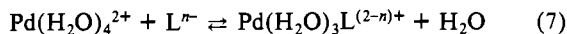
Me_2SO and other sulfoxides are in general poor entering ligands in reactions with platinum complexes.^{32,33} For instance, the rate of substitution of one water molecule for Me_2SO on $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ is only about twice the water-exchange rate on the tetraaqua complex.⁶ This is rather surprising, since ligands coordinating via sulfur atoms are generally also good entering groups, at least when the sulfur is readily accessible. Steric hindrance is probably not a major reason for the low nucleophilicity of Me_2SO , because the molecule has a pyramidal structure with the sulfur atom at the top,^{25–29,31} not very crowded. This low efficiency as a nucleophile has previously been ascribed to the polarity of the Me_2SO molecule.³² The sulfur carries positive partial charge and the oxygen a correspondingly negative charge.³⁴ It has been suggested that a possible consequence of this charge separation might be that the initial bonding to platinum takes place through the oxygen and that a subsequent rapid intramolecular isomerization to S-bonding could occur between the bond-making transition state and

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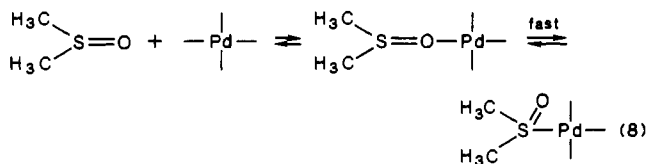
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a five-coordinate intermediate.³³

In the case of palladium, rate constants for reaction 7 are listed in Table II for a series of entering ligands L. The large spread



in the k_1 values speaks in favor of an associative mode of activation. The replacement of a water molecule by Me_2SO is much slower than the rate of substitution of water for halides, which is contrary to the expectation for a sulfur-bonded ligand. A mechanism similar to that proposed for the formation of Me_2SO complexes of platinum(II)³³ might be operating (eq 8), with the rate-de-



termining formation of an oxygen-bonded form, followed by a rapid intramolecular isomerization to the thermodynamically more stable sulfur-bonded complex. The experiments so far give no conclusive support of such a mechanism, however. The rate constant for substitution with Me_2SO is ca. 12 times smaller than the water-exchange rate constant, without taking possible statistical factors into account. From the above discussion, it follows that Me_2SO is an even poorer nucleophile in the case of palladium than in the case of platinum.

The activation entropies for both forward and reverse processes, listed in Table I, have large negative values, in accord with the attribution of the associative mode of activation anticipated. The two corresponding volumes of activation are negative also. However, the large value of ΔV^\ddagger_1 cannot be immediately interpreted as a support for a strong associative character of reaction 1. For unsymmetrical reactions, the partial molar volumes of the

reactants and products can be very different. A closer inspection of the volume profile of the overall reaction is necessary before definite mechanistic conclusions can be drawn. In the present case, the volume profile of Figure 6 shows that the volume of the transition state is much smaller than the volume which would result from a smooth change along the reaction coordinate (Figure 6, dashed line), suggesting a strongly associative reaction. This is even more so, since formation of a fifth bond in a trigonal-bipyramidal transition state is expected to be accompanied by some axial bond lengthening, which will produce a positive contribution to the volume of activation. If the reaction takes place via an intermediate O-bonded complex, however, the interpretation of the volume changes will be even more complicated.

In conclusion, although an associative mode of activation can undoubtedly be assigned to the forward as well as to the reverse process of reaction 1, an evaluation of their degree of associative character must be postponed until more volumes of activation are collected for similar simple reactions of square-planar complexes.

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Registry No. $\text{Pd}(\text{H}_2\text{O})_4^{2+}$, 22573-07-5; $\text{Pd}(\text{Me}_2\text{SO})(\text{H}_2\text{O})_3^{2+}$, 107913-44-0; $\text{Pd}(\text{Me}_2\text{SO})_2(\text{H}_2\text{O})_2^{2+}$, 107913-45-1; Me_2SO , 67-68-5.

Supplementary Material Available: Spectrophotometric equilibrium measurements at 298 K and ambient pressure (Table SI) and at variable pressure (Table SII), NMR measurements at variable temperature (Table SIII), observed rate constants at ambient pressure for excess palladium at 298 K (Table SIV), for excess Me_2SO at various temperatures (Table SV), and for excess Me_2SO at various pressures (Table SVI) (6 pages). Ordering information is given on any current masthead page.

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Variable-Temperature, -Pressure, and -Frequency Oxygen-17 NMR Study of Water Exchange on Hexaaquatitanium(III): A Limiting Associative Mechanism?^{1,2}

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Water exchange on hexaaquatitanium(III) has been studied as a function of temperature (249–369 K) and pressure (up to 235 MPa, at several temperatures) by oxygen-17 FT-NMR spectroscopy at 1.4, 4.7, and 8.4 T. The samples, in up to 20% ¹⁷O-enriched H_2O , contained Ti^{3+} (~0.3 M), H^+ (2.0–3.0 M), and trifluoromethanesulfonate as noncoordinating counterion. The following kinetic parameters were obtained: $k_{\text{ex}}^{298} = (1.81 \pm 0.03) \times 10^5 \text{ s}^{-1}$, $\Delta H^\ddagger = 43.4 \pm 0.7 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = +1.2 \pm 2.2 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta V_0^\ddagger = -12.1 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$, and $\Delta\beta^\ddagger = -(1.9 \pm 0.4) \times 10^{-2} \text{ cm}^3 \text{ mol}^{-1} \text{ MPa}^{-1}$. This volume of activation is the most negative value measured so far for a water-exchange reaction on a hexaaqua ion and is close to the value of $-13.5 \text{ cm}^3 \text{ mol}^{-1}$ suggested by Swaddle⁴ for a limiting associative A mechanism. These results are discussed together with available data for complex formation reactions involving hexaaquatitanium(III).

Introduction

The study of the effect of pressure on the rate of a chemical reaction has become an important aid in mechanistic elucidation in recent years.^{4,5} It has been shown to be particularly useful for a better understanding of the dynamics of exchange at solvated metal ions, the ubiquitous precursors of metal complexes in so-

lution. For example, the high-pressure oxygen-17 NMR study of water exchange on divalent metal ions across the first-row transition-metal series allowed us to demonstrate the unpredicted changeover from associative interchange I_a to dissociative interchange I_d mechanisms along the series.^{6,7} This changeover has been rationalized in terms of steric effects due to changes in ionic radius and of filling of d orbitals: increasing e_g antibonding electron population favors dissociation, and increasing t_{2g} "between-bond" electron population disfavors association.

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