Variable-temperature and Variable-pressure ^1H NMR Studies of Dimethylsulfide Exchange on *trans*-bis(dimethylsulfide)dichloropalladium(II) in Various Solvents [1]

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The rate-law, temperature and pressure dependences for the ligand exchange reaction of dimethylsulfide on $Pd(Me_2S)_2Cl_2$ *were measured by* ^1H *NMR in the solvents chloroform, dichloromethane, o-dichlorobenzene and benzonitrile. The respective experimental* ΔH^*, ΔS^* *and* ΔV^* *values are: 38.5 kJ* mol^{-1}, -69.7 *J* K^{-1} mol^{-1} *and* -7.1 cm^3 mol^{-1}*; 33.4, −85.6 and −8.4; 36.1, −70.2 and −7.2; 38.1, −67.4 and −5.4. The experimental* ΔV^* *were correlated to the solvent electrostriction parameter* q_p *leading to a value of* -5.9 ± 1.6 cm^3 mol^{-1} *for* ΔV^*_{int}*, and a very small* ΔV^*_{solv} *contribution. The activation parameters and the second order rate law lead to the assignment of a highly symmetrical associative ligand exchange pathway with a trigonal bipyramidal transition state or intermediate, without charge separation or important dipole formation during the activation process.*

Introduction

The volume of activation ΔV^* (which is obtained from the study of the effect of pressure on the rate constant) is considered nowadays as being an important parameter for the assignment of reaction mechanisms in solution [4]. It is generally accepted that ΔV^* consists of two components, *i.e.*, the intrinsic part, ΔV^*_{int}, resulting from changes in internuclear distances within the reactants during the formation of the transition state, and the solvation part, ΔV^*_{solv}, consisting mainly in electrostrictive effects. We can therefore consider:

$$\Delta V^* = \Delta V^*_{int} + \Delta V^*_{solv} \qquad (1)$$

The ΔV^*_{int} term is very effective for the diagnosis of mechanisms. However, its use is restricted by the possibility to separate it from the solute–solvent interaction term, ΔV^*_{solv}, which may become very important in non-polar solvents [5]. Kotowski *et al.* [6] studied reaction (2) conductimetrically as a function of pressure in different solvents. They observed a good linear correlation between ΔV^* and the solvent electrostriction parameter q_p. This parameter is obtained from the pressure derivative of ΔG^*_{solv} in the Kirkwood equation, and describes the solvent in terms of the pressure derivative of its dielectric constant according to eqn. (3). The intercept as $q_p = 0$ gave ΔV^*_{int} in an hypothetical non-solvating mechanism. The important ΔV^*_{solv} contributions observed in the different solvents were interpreted in terms of large changes in polarity or charge formations during the formation of the transition state.

$$trans\text{-}Pt(py)_2Cl(NO_2) + py \rightarrow trans\text{-}Pt(py)_3(NO_2)^+ + Cl^- \qquad (2)$$

$$q_p = [3/(2\epsilon + 1)^2]/(\delta\epsilon/\delta P)_T \qquad (3)$$

According to this interpretation a reaction with no important change in polarity or charge formations during the activation process must have a negligible ΔV^*_{solv} contribution, with $\Delta V^* \cong \Delta V^*_{int}$. To verify this we have studied the neutral exchange reaction (4) by high pressure proton NMR in solvents of different polarities.

$$trans\text{-}Pd(Me_2S)_2Cl_2 + {}^*Me_2S \rightleftarrows trans\text{-}Pd(Me_2S)({}^*Me_2S)Cl_2 + Me_2S \qquad (4)$$

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Experimental

Materials

All solvents used (Fluka, Puriss and CIBA-GEIGY for the deuterated solvents) were stored over 4 Å activated molecular sieves (Merck) in dark bottles. $CHCl_3$ was previously treated with $CaCl_2$ for several days in the dark and distilled twice. CH_3NO_2 was first dried with Na_2SO_4 and also distilled twice. The complex *trans*-$Pd(Me_2S)_2Cl_2$ was prepared according to Roulet and Barbey [7]. The dimethylsulfide (Fluka, Puriss) was used as received and K_2PdCl_4 was donated by Prof. R. Roulet. The solutions for NMR measurements were prepared by weight, and in the case of nitromethane they were prepared in a glove-box (water < 3 ppm). The concentration in complex was between 0.04 and 0.10 mol per kg of solvent, and the concentration of Me_2S was approximately double that of the complex. About 3% w/w TMS was added as an internal reference.

^{1}H-NMR Measurements

Variable temperature measurements were performed on a Bruker WP-60 spectrometer using either an internal deuterium lock ($CHCl_3/CDCl_3$ 1:1, CH_2Cl_2/CD_2Cl_2 1:1, CH_3NO_2/CD_3NO_2 1:1) or an external ^{19}F lock (o-$C_6H_4Cl_2$, C_6H_5CN). The temperature was measured by a substitution technique using a 100 Ω Pt resistor [8].

Variable pressure measurements were run on the same spectrometer using a slightly modified version [9] of a high pressure probe head [10]. An external ^{19}F lock was used.

Data Treatment

To minimize the effect of instrumental line broadening, the line widths w_i (i: coordinated or free) were taken as

$$w_i = w_i^{measd} - w_{TMS}^{measd} \qquad (5)$$

where w^{measd} is the measured width on the spectrum. Line widths in the absence of dimethylsulfide exchange w_i^o were determined at low temperature, where the reaction is frozen on the NMR time scale.

In the slow-exchange region the residence time of the site i is given by

$$1/\tau_i = \pi(w_i - w_i^o) \qquad (6)$$

In the case of intermediate and rapid exchange the rate constants were obtained by least-squares curve fittings with the program EXCHIT [11]. This program is derived from the program ECHGNC [12] based on the Kubo-Sack stochastic theory.

Results

At low temperatures 1:2 molar ratio solutions of *trans*-$Pd(Me_2S)_2Cl_2$ and Me_2S in chloroform, dichloromethane, o-dichlorobenzene and benzonitrile show only two singlets of equal intensity corresponding to the coordinated (δ_{trans} = 2.43, 2.39, 2.21, 2.38 ppm respectively) and free (δ_{free} = 2.15, 2.10, 1.93, 2.01 ppm) dimethylsulfide. In nitromethane, there is evidence of a small amount of *trans–cis* interconversion (δ_{cis} = 2.45 ppm, δ_{trans} = 2.38 ppm, δ_{free} = 2.08 ppm). The isomerisation equilibrium constant is temperature dependent, the *trans* isomer being favored with increasing temperature (K = [*trans*]/[*cis*]: 7.5 at 247 K, 8.2 at 257 K, 10.9 at 269 K). The interconversion into the more polar *cis* form observed in the polar solvent nitromethane is not surprising. Such equilibria had been observed previously for the platinum analog $Pt(Me_2S)_2Cl_2$ (K = 6.4 at 302 K in $CHCl_3$ and K = 1.88 at 301 K in CH_2Cl_2), with similar temperature and polarity dependence [7].

In the absence of the *cis* isomer the coalescence of the signals of *trans*-coordinated and free dimethylsulfide leads to the rate constants for the ligand exchange reaction (4). It has been shown previously that in $CDCl_3$ [7] the rate law is first order in both complex and free ligand according to eqns. (7) and (8):

$$\frac{1}{\tau_{trans}} = -\frac{d[trans\text{-}Pd(Me_2S)_2Cl_2]}{[trans\text{-}Pd(Me_2S)_2Cl_2]\,dt} = k[Me_2S] \qquad (7)$$

$$\frac{1}{\tau_{Me_2S}} = -\frac{d[Me_2S]}{[Me_2S]\,dt} = k[trans\text{-}Pd(Me_2S)_2Cl_2] \qquad (8)$$

where τ_{trans} and τ_{Me_2S} are the mean lifetimes of the complex and the free ligand. These mean lifetimes are related to the residence times of *trans* coordinated τ_{trans}^r and free dimethylsulfide $\tau_{Me_2S}^r$, as obtained by NMR, by the following relations:

$$\tau_{trans}^r = 2\tau_{trans} \qquad (9)$$

$$\tau_{Me_2S}^r = \tau_{Me_2S} \qquad (10)$$

The rate constants and activation parameters are given in Table I. The activation enthalpies ΔH^* and entropies ΔS^* were obtained from the Eyring equation by a linear least-squares treatment (see Fig. 1). The volumes ΔV^* of activation were calculated using the equation:

$$\ln k = \ln k_0 - \Delta V_0^* P/RT + \Delta\beta^* P^2/2RT \qquad (11)$$

In quadratic fits the compressibility coefficients of activation $\Delta\beta^*$ are equal to zero, within experi-

TABLE I. Rate Constants and Activation Parameters for Dimethylsulfide Exchange on Pd(Me$_2$S)$_2$Cl$_2$ in Different Solvents.[a]

Solvent	k_{ex}^{298} (m^{-1} s^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (JK^{-1} mol^{-1})	ΔV^* (cm^3 mol^{-1})	q_p[b] (10^5 MP a^{-1})
$CHCl_3$	260 ± 8	38.5 ± 1.4	−69.7 ± 4.5	−7.1 ± 0.5 (308.2 K)	16.7
CH_2Cl_2	300 ± 12	33.4 ± 2.6	−85.6 ± 8.8	−8.4 ± 0.3 (296.2 K)	11.5
o-$C_6H_4Cl_2$	624 ± 22	36.1 ± 1.7	−70.2 ± 5.9	−7.2 ± 0.6 (287.0 K)	6.83
C_6H_5CN	393 ± 14	38.1 ± 1.0	−67.4 ± 3.4	−5.4 ± 0.1 (298.3 K)	1.81

[a] Errors quoted are one standard deviation (ΔV^*) or standard errors with a confidence level of 95% (k_{ex}^{298}, ΔH^*, ΔS^*). [b] Solvent electrostriction parameters from [6] and [13].

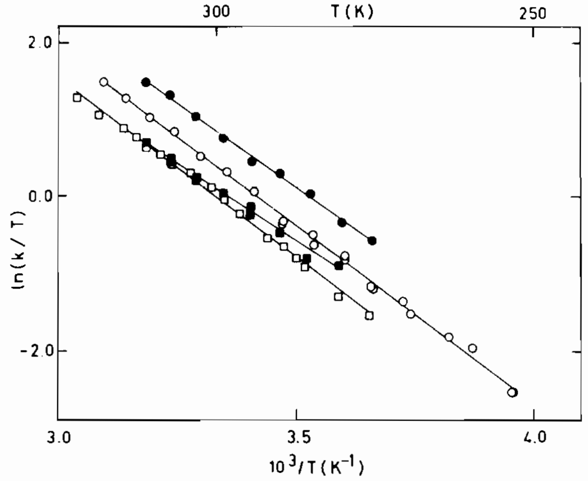

Fig. 1. Plot of ln(k/T) *versus* reciprocal temperature in the various solvents: □ $CHCl_3$, ■ CH_2Cl_2, ● o-$C_6H_4Cl_2$, ○ C_6H_5-CN.

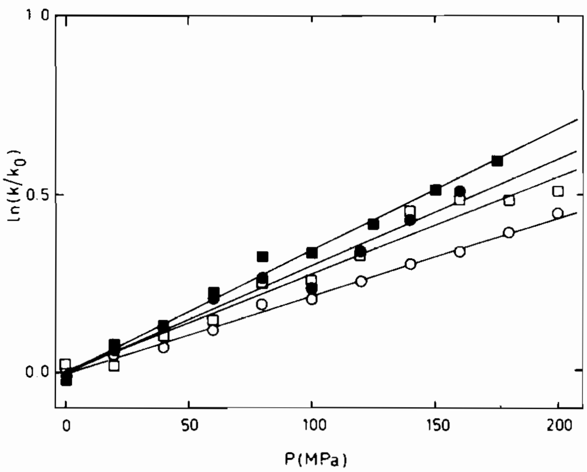

Fig. 2. Plot of ln(k/k$_0$) *versus* pressure in the various solvents: ■ $CHCl_3$, □ CH_2Cl_2, ● o-$C_6H_4Cl_2$, ○ C_6H_5CN.

mental error (10^2 $\Delta\beta^*$: −0.7 ± 0.8 in CH_2Cl_3, −0.8 ± 0.6 in CH_2Cl_2, +0.6 ± 1.3 in o-$C_6H_4Cl_2$, and 0.0 ± 0.3 cm^3 mol^{-1} MPa^{-1} in C_6H_5CN). Therefore the second order term in eqn. (8) was neglected and linear fits were used (see Fig. 2).

In nitromethane, the kinetic behaviour is more difficult to analyse. Dimethylsulfide exchange occurs between three sites: the small amount of *cis*, the *trans* and the free. We were not able to separate the three possible rate constants, as a function of temperature and pressure, in order to obtain the activation parameters for the three pathways: isomerization, ligand exchanges on *cis*- and *trans*-complex. However, it is clear from the spectra that the ligand exchange on the *cis* complex is at least five times faster than the two other processes. It is not blocked at the NMR time scale even at 235 K.

Discussion

Investigations of substitution reactions on square-planar complexes have been described mainly for Pt(II) compounds. The limited data available for reactions on Pd(II) complexes are however sufficient to show the typical associatively-activated behaviour of square-planar substitution, with the usual two term rate law: rate = k_1[complex] + k_2[complex] [nucleophile]. The second term represents the direct attack of the nucleophile, while the first one represents the solvolysis path in which a solvent-containing intermediate is formed and subsequently undergoes a rapid substitution [14]. For the exchange reaction (4) of Me_2S on $Pd(Me_2S)_2Cl_2$ it has been shown previously (in chloroform) that the rate law is simply first order in both complex and free ligand, *i.e.* without a solvolytic pathway. We have checked the

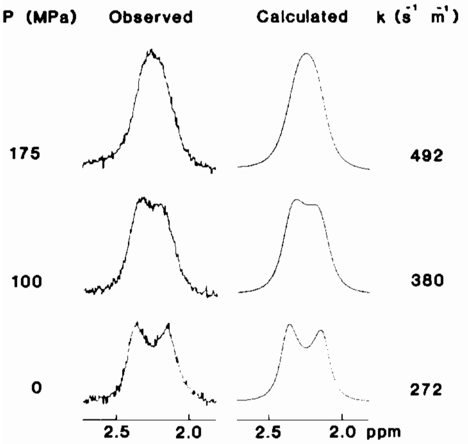

Fig. 3. Observed and calculated ^{1}H NMR spectra for the ligand exchange *trans*-Pd(Me$_2$S)$_2$Cl$_2$ + *Me$_2$S $\rightleftarrows$ *trans*-Pd(Me$_2$S)(*Me$_2$S)Cl$_2$ + Me$_2$S as a function of pressure in CH$_2$Cl$_2$ at 269.2 K.

absence of this latter pathway for the solvent with the highest nucleophilicity used in this study, benzonitrile. The observed rate constants obtained at 298 K were the following: 404 m^{-1} s^{-1} (0.044 m Pd(Me$_2$S)$_2$Cl$_2$, 0.079 m Me$_2$S), 386 m^{-1} s^{-1} (0.082 m, 0.135 m), 396 m^{-1} s^{-1} (0.087 m, 0.213 m). The constant values obtained allowed us therefore to neglect the solvolytic path.

The values of the observed second order rate constants in different solvents (see Table I) are similar and do not correlate either with the dielectric constants or the electrostriction parameters q_p of the solvents. The activation enthalpies ΔH* and entropies ΔS* are solvent independent, with the possible exception of the least accurate values obtained in CH$_2$Cl$_2$. Figure 3 shows the effect of pressure on the ^{1}H-NMR spectra for the exchange reaction in CH$_2$Cl$_2$. During these experiments the temperature was kept constant and the pressure increased to 175 MPa (1 MPa = 10 bars). The coalescence of the signals (the increase in exchange rate) with increasing pressure is characteristic of a bond-making process. The values of the activation volumes are similar, indicating only small solvent effects on the mechanism (if any). The rate law and the negative ΔS* and ΔV* suggest an associative process, proceeding through a pentacoordinated transition state (I_a mechanism) or intermediate (A mechanism).

As mentioned in the Introduction, it is assumed that the substitution reaction (2) of *trans*-Pt(py)$_2$-Cl(NO$_2$) by pyridine occurs through a highly polar or charged transition state with important solute–solvent interactions. The extent of the interactions is clearly shown by the relation between ΔV* and the electrostriction parameters q_p (see Fig. 4). Roulet and Barbey [7] assumed that the exchange of dimethylsulfide on Pt(Me$_2$S)$_2$Cl$_2$ occurs through the strongly polar ion-paired square pyramidal intermediate {[Pt(Me$_2$S)$_3$Cl]$^+$Cl$^-$}. They were able to prepare [Pt(Me$_2$S)$_3$Cl]BF$_4$, a salt of the proposed intermediate. For the exchange of dimethylsulfide on Pd(Me$_2$S)$_2$Cl$_2$, we did not observe a significant dependence of ΔV* with the solvent. A linear fit of ΔV* as a function of q_p leads to an intercept value of −5.9 ± 1.6 cm^3 mol^{-1}, the intrinsic volume of activation in a hypothetical non solvating solvent, and a slope of −13 ± 15 cm^3 mol^{-1} kPa. The value of ΔV^*_{int} is close to the value of −4 ± 1 cm^3 mol^{-1} obtained for reaction (2). The relatively small absolute value may result from some loosening of the non-exchanging bond that must occur in order to accomodate the incoming ligand, thus cancelling out some of the volume decrease due to bond formation. The slopes of the lines in Fig. 4 are related to the change in dipole moment during the activation process [6]. For the substitution on *trans*-Pt(py)$_2$-Cl(NO$_2$) the dipole moment of the transition state was determined at *ca.* 11 Debye, whereas for the exchange on *trans*-Pd(Me$_2$S)$_2$Cl$_2$ we obtain a value of only 3 ± 4 Debye, assuming the same average radius for the transition state. This suggests a highly symmetrical exchange pathway with a trigonal bipy-

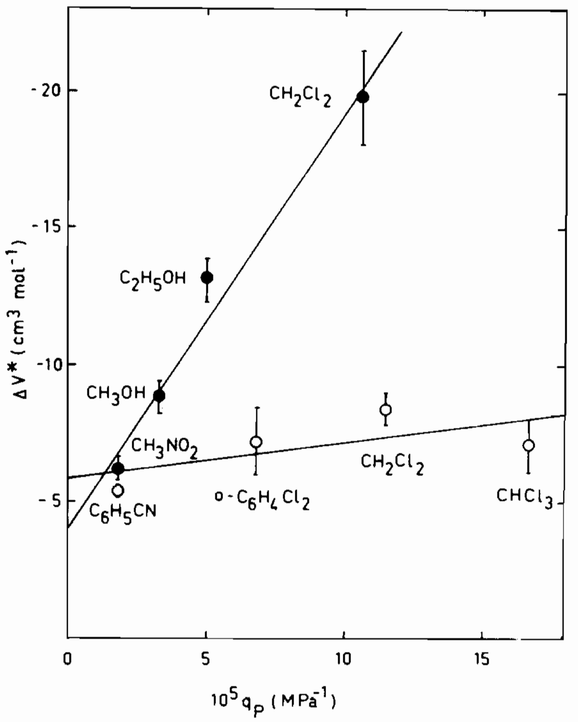

Fig. 4. Plot of ΔV* *versus* the solvent electrostriction parameter q_p for the substitution of *trans*-Pt(py)$_2$Cl(NO$_2$) with pyridine (●) [6] and for the dimethylsulfide exchange on *trans*-Pd(Me$_2$S)$_2$Cl$_2$ (○).

ramidal transition state or intermediate, with the entering and leaving groups in the trigonal plan and the chlorides in axial position. This highly symmetrical pathway, with small electrostrictive changes, is further supported by the absence of pressure dependence of ΔV^* ($\Delta\beta^* \cong 0$, see Fig. 2) observed for this reaction.

It should be added that the Pd(II) exchange reaction is about 10^5 times faster than the exchange of the Pt(II) analog [7]. This generally observed difference in lability between the complexes of these two ions was associated to a much weaker Pd–ligand bond strength [16]. Another consideration (based on the comparison between the study of Roulet and Barbey and ours) could be a higher free energy requirement to reach a more polar or charge separated transition state in the case of Pt(II).

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