K_1 and K_2 as in eq 4. The value of k_4 is 1.9 M^{-1} s^{-1}. Both schemes indicate that pentacyano and hexacyano complexes exist in basic aqueous solution and that their stability constants are not very large.

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Registry No. $Ni^{III}(CN)_4(H_2O)_2^-$, 97011-73-9; $Ni^{III}(CN)_6^{3-}$, 97011-80-8; $Ni^{III}(^{13}CN)_4(H_2O)_2^-$, 117226-39-8; $Ni^{III}(CN)_4(NCO)_2^{3-}$, 97011-79-5; $Ni^{III}(CN)_4(Cl)_2^{3-}$, 54003-01-9; $Ni^{III}(NCCH_3)_2^-$, 97011-77-3; $Ni^{III}(py)_2^-$, 97011-76-2; $Ni^{III}(N_3)_2^{3-}$, 97011-78-4; $Ni^{III}(imid)_2^-$, 97011-75-1; $Ni^{III}(bpy)_2^-$, 117226-40-1; $Ni^{II}(CN)_4^{2-}$, 48042-08-6; OCN^-, 661-20-1; HCN, 74-90-8; H_2O_2, 7722-84-1; CN^-, 57-12-5.

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Solvent Dependence of the Activation Parameters for the Solvolysis of a Square-Planar Complex, (Pyridine)(pentamethyldiethylenetriamine)palladium(II)

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The solvolysis reaction of $Pd(Me_5dien)py^{2+}$ was studied as a function of temperature and pressure in the solvents H_2O, MeOH, EtOH, Me_2SO, DMF, and MeCN in order to gain insight into the solvent dependence of this process. The selected system involves the release of a neutral ligand, which reduces possible contributions from electrostriction and thus enables an estimation of the intrinsic component of the activation parameters. The activation entropy is negative throughout, and the activation volume varies between 0 and −6 cm^3 mol^{-1}, characteristic for an associative substitution process.

Introduction

We have a longstanding interest in the substitution mechanisms of sterically-hindered square-planar complexes of Pt(II) and Pd(II).[2] These studies have emphasized the significance of spontaneous solvolysis reactions and their integrated role in the substitution behavior of such complexes.[3] For a series of diethylenetriamine (dien) and substituted dien complexes of Pd(II), we demonstrated that although a severe increase in steric hindrance can slow down the solvolysis process in aqueous solution by up to 6 orders of magnitude, it does not affect the fundamental associative nature of the substitution process.[4] For a particular leaving group, vis. Cl^-, the increase in steric hindrance is accompanied by an increase in $\Delta H^\ddagger$, whereas $\Delta S^\ddagger$ and $\Delta V^\ddagger$ remain constant and strongly negative throughout the series of complexes. Later work[5,6] demonstrated that these parameters, especially $\Delta V^\ddagger$, depend significantly on the nature of the leaving group. For instance, more negative $\Delta V^\ddagger$ values (between −8 and −16 cm^3 mol^{-1}) were found for anionic leaving groups (viz. Cl^-, Br^-, N_3^-, $C_2O_4^{2-}$, CO_3^{2-}), compared to values around −3 cm^3 mol^{-1} for neutral leaving groups such as NH_3 and pyridine (py). This difference was ascribed to solvational changes caused by changes in dipole moment during a square-pyramidal to trigonal-bipyramidal transition in the associative transition state. In this way anionic leaving groups will cause more negative $\Delta V^\ddagger$ values, and the value found for neutral leaving groups (viz. −3 cm^3 mol^{-1}) most probably represents the intrinsic volume collapse associated with the overall associative attack of a water molecule.[7] This intrinsic value is significantly smaller than that predicted and observed for associative aquation of octahedral complexes.[8-11]

In order to throw more light on the intimate nature of such solvolysis reactions of square-planar complexes, we have studied the solvent dependence of the activation parameters for the solvolysis of $Pd(Me_5dien)py^{2+}$, i.e., a sterically hindered complex with a neutral leaving group. In general, little is known about the solvent dependence of these parameters,[2] and the data enable us to comment on the intrinsic factors that control these parameters.

Experimental Section

The $[Pd(1,1,4,7,7\text{-}Me_5dien)py](ClO_4)_2$ complex was prepared according to the following procedure. Concentrated pyridine was added to a 10^{-2} M solution of the corresponding aqua complex[12] in a 5:1 ratio, and the reaction mixture was slowly concentrated to a very small volume on a water bath. A light yellow crystalline product separated on cooling the mixture in an ice bath. The product was recrystallized from a 0.1 M aqueous pyridine solution in the same way as described above. The crystals were filtered off, washed with small quantities of ice cold water and ethanol, and dried in a vacuum desiccator. Microanalyses[13] were in good agreement with the theoretically expected values. The complex and its solvolysis products were characterized from their UV–vis spectra recorded on Perkin-Elmer 555 and Shimadzu UV 250 spectrophotometers.

The solvents MeOH, EtOH, Me_2SO, DMF and MeCN were purified and dried according to standard procedures.[14] Chemicals of analytical reagent grade and doubly deionized water were used throughout this study. The reactions at ambient pressure were followed in either the thermostated (±0.1 °C) cell compartment of a Zeiss DMR 10 spectrophotometer or a thermostated (±0.1 °C) Aminco stopped-flow system. At elevated pressure, a thermostated (±0.1 °C) high-pressure cell[15] and a self-constructed high-pressure stopped-flow system[16] were employed. All kinetic measurements were performed under pseudo-first-order conditions and a linearity standard of between 2 and 3 half-lives was set for

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(1) (a) Experimental work performed at the Institute for Physical Chemistry, University of Frankfurt, FRG. (b) On leave from the University of Peshawar, Pakistan. (c) On leave from the University of the Orange Free State, South Africa.

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the corresponding first-order plots. The reactions were followed at a wavelength corresponding to the maximum absorbance change.

Table I. k_{obs} as a Function of Solvent, Temperature, and Pressure for the Solvolysis of $Pd(Me_5dien)py^{2+}$ [a]

solvent	[ptsa] or $[OH^-]$, M	temp, °C	pressure, MPa	10^3k_{obs}, s^{-1}
EtOH[b]	0.1	16.0	0.1	0.39 ± 0.03
		20.0		0.69 ± 0.03
		25.0		1.25 ± 0.02
	0.01	25.0		1.24 ± 0.02
	0.1	30.0		1.98 ± 0.03
		35.0		4.06 ± 0.05
		25.0	5	1.23 ± 0.01
			25	1.27 ± 0.02
			50	1.33 ± 0.03
			75	1.38 ± 0.01
			100	1.44 ± 0.03
MeOH[b]	0.005	25.0	0.1	1.19 ± 0.02
	0.01			1.00 ± 0.03
	0.1			1.02 ± 0.03
		30.0		1.90 ± 0.02
		35.0		2.88 ± 0.01
		40.0		5.33 ± 0.03
		25.0	5	1.03 ± 0.03
			25	1.11 ± 0.04
			50	1.21 ± 0.03
			75	1.27 ± 0.04
			100	1.35 ± 0.03
			125	1.37 ± 0.02
			150	1.50 ± 0.01
H_2O[c]	0.01	15.0	0.1	0.320 ± 0.007
		20.0		0.571 ± 0.009
		25.0		1.04 ± 0.02
	0.05			1.05 ± 0.02
	0.1			1.11 ± 0.03
	0.01	33.0		2.15 ± 0.02
		40.0		3.35 ± 0.03
		25.0	5	1.00 ± 0.02
			25	1.02 ± 0.02
			50	1.06 ± 0.02
			75	1.09 ± 0.03
			100	1.11 ± 0.02
			125	1.16 ± 0.03
			150	1.20 ± 0.04
Me_2SO[b]	0.1	15.0	0.1	2.49 ± 0.08
		20.0		4.64 ± 0.03
		25.0		7.40 ± 0.08
		30.0		12.7 ± 0.3
	0.01			12.6 ± 0.3
	0.005			13.1 ± 0.5
	0.1		5	13.8 ± 0.4
			20	13.7 ± 0.4
			40	13.9 ± 0.5
			60	13.7 ± 0.3
			80	13.9 ± 0.4
		35.0	0.1	17.8 ± 1.1
		40.0		27.2 ± 0.5
DMF[b]	0.1	15.0	0.1	5.1 ± 0.2
		20.0		8.0 ± 0.1
		25.0		11.7 ± 0.2
		30.0		19.8 ± 0.2
		35.0		30.2 ± 0.4
		30.0	5	24.2 ± 0.6
			25	25.2 ± 0.9
			50	25.5 ± 1.2
			75	26.9 ± 0.9
			100	27.6 ± 0.6
MeCN[b]	0.1	20.0	0.1	186 ± 1
		25.0		251 ± 8
		30.5		467 ± 13
		36.5		694 ± 12
		30.0	5	433 ± 13
			25	456 ± 12
			50	471 ± 12
			75	468 ± 12
			100	481 ± 15

[a] [Pd] = (2–5) × 10^{-4} M. [b] Reaction in the presence of ptsa. [c] Reaction in the presence of OH^-.

Table II. Spectral Data for the Solvolysis of $Pd(Me_5dien)py^{2+}$

	$Pd(Me_5dien)py^{2+}$		$Pd(Me_5dien)S^{2+}$	
solvent	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
H_2O	307	1150	326	1174[a]
MeOH	307	1100	333	1050
EtOH	308	1080	337	1010
Me_2SO	309	1280	338	1290
DMF	308	1250	334	1310

[a] Reference 5 and this work.

Results and Discussion

It was the objective of this study to measure the activation parameters for reaction 1 as a function of the solvent (S). Since

$$Pd(Me_5dien)py^{2+} + S \xrightarrow{k_1} Pd(Me_5dien)S^{2+} + py \qquad (1)$$

it is well-known that the produced solvento complexes are extremely labile,[12] some precautions had to be taken to prevent the reverse substitution process, i.e., anation when S = H_2O. This can be done in two ways depending on the nature of S. In the case of S = H_2O, reaction 1 is performed in basic medium (pH >9) where the aqua complex is immediately deprotonated to the nonlabile hydroxo species,[17] and no reverse substitution reaction occurs. Care must, however, be taken for a possible contribution toward k_{obs} resulting from the direct attack of the substrate by hydroxide, i.e., the k_2 path in (2).[5] For the temperature and

$$k_{obs} = k_1 + k_2[OH^-] \qquad (2)$$

pressure dependence study a base concentration of 0.01 M was selected, since under such conditions $k_{obs} \approx k_1$ (see Table I). This procedure could not be adopted for the other solvents due to the insolubility of the base, and in these cases pyridine was protonated with *p*-toluenesulfonic acid (ptsa) to prevent the reverse reaction. Under such conditions the expression for k_{obs} based on reactions 1 and 3 is given by (4), where k_{-1} represents the rate constant

$$py + H^+ \overset{K}{\rightleftharpoons} pyH^+ \qquad (3)$$

$$k_{obs} = k_1 + k_{-1}K[\text{total py}]/(K + [H^+]) \qquad (4)$$

for the reverse step in reaction 1. It follows that at high enough $[H^+]$, i.e., where all the released py is protonated, rate law 4 simplifies to $k_{obs} = k_1$. The data in Table I clearly demonstrate that k_{obs} is independent of $[H^+]$ in the range $0.01 \leq [\text{ptsa}] \leq 0.1$ M, and therefore the temperature and pressure dependence studies were performed at [ptsa] = 0.1 M. At [ptsa] < 0.01 M the reverse reaction interferes meaningfully, which results in a significantly higher value of k_{obs} and deviation from first-order behavior due to the absence of an excess of py.

In this respect it should be noted that ptsa is a monohydrate, which brings about a water concentration of ca. 0.1 M at [ptsa] = 0.1 M. Various experiments were undertaken to clarify the influence of this water content on the studied reactions. In the first place the reaction in MeOH was repeated by acidifying with concentrated H_2SO_4 to 0.01 and 0.05 M. In this way the water content was 0.002 and 0.007 M, respectively. The spectral changes and observed rate constants were identical with those observed with 0.1 M ptsa. Addition of H_2O up to 4 M to the final product mixture caused a shift in the absorption maximum from 332 to 324 nm, which corresponds with the change from $Pd(Me_5dien)MeOH^{2+}$ to $Pd(Me_5dien)H_2O^{2+}$ (see Table II). Similar results were observed for Me_2SO.

In another series of experiments we succeeded in isolating the complex $[Pd(MeEt_4dien)H_2O](ClO_4)_2$ as a solid. The spectrum of this complex was measured in different solvents, and due to a relatively fast exchange of solvent molecules, the product spectra were in close agreement with those reported in Table II. Furthermore, addition of H_2O up to 2 M resulted in a mixture of the aqua and solvento species, and up to 4 M water was required to

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Table III. Summary of Rate and Activation Parameters for the Solvolysis of $Pd(Me_5dien)py^{2+}$ as a Function of Solvent at 25 °C and 0.1 M ptsa

solvent	$10^5 k_1$, $M^{-1}\ s^{-1}$	ΔH^{*}, kJ mol^{-1}	ΔS^{*}, J $K^{-1}\ mol^{-1}$	ΔV^{*}, $cm^3\ mol^{-1}$
EtOH	7.4 ± 0.1	86 ± 3	−38 ± 11	−4.1 ± 0.1
MeOH	4.1 ± 0.1	87 ± 4	−39 ± 14	−6 ± 1
H_2O	1.87 ± 0.04[a]	69 ± 4	−105 ± 14	−3.1 ± 0.1
Me_2SO	52.8 ± 0.6	69 ± 2	−78 ± 8	≈0
DMF	90.1 ± 1.5	63 ± 2	−91 ± 7	−3.4 ± 0.3[b]
MeCN	1310 ± 42	60 ± 5	−77 ± 17	−2.4 ± 0.6[b]

[a] k_1 value for solvolysis during the reaction with OH^-. [b] Temperature = 30 °C.

convert the solvento species completely into the aqua form. Thus it follows that the water introduced with the addition of 0.1 M ptsa will have no significant effect on the solvolysis reactions under investigation.

The temperature and pressure dependencies of k_1 as a function of solvent (Table I) were used to calculate the activation parameters (ΔH^*, ΔS^*, and ΔV^*) in the usual way,[11] and the results are summarized in Table III. For these calculations, k_1 was converted to a second-order rate constant in order to take the different solvent concentrations into consideration. The reactivity sequence $H_2O < MeOH < EtOH < Me_2SO < DMF < MeCN$ is in good agreement with that reported for solvolysis reactions of sterically unhindered Pt(II) and Pd(II) complexes, viz. k_1 is usually larger for dipolar aprotic than for protic solvents.[18-20] On the contrary, a reverse reactivity order ($H_2O > MeOH > Me_2SO$) was reported for solvolysis of the sterically hindered $Pd(Et_4dien)X^+$ complexes.[21-23] The chemical shifts of the methyl protons indicated that smaller solvent molecules can interact better with the crowded Pd(II) center than the larger ones. It was suggested on the basis of the ΔS^* values that solvolysis is associative for water as solvent but dissociative for Me_2SO and DMF as solvents.[23] However, in later work[21] the error limits of the ΔS^* data were taken into account and the results (including ΔV^* data) were interpreted in terms of an I_a mechanism. The present data, however, exhibit a good agreement with data for nonhindered systems, and there is no reason to believe that a change in mechanism is at hand.

The values of ΔV^* in Table III are all small and slightly negative and do not exhibit a specific trend with the nature of the solvent. The solvation of the $Pd(Me_5dien)py^{2+}$ complex in the ground and transition states is expected to be very similar, since the entering and leaving groups are neutral and no substantial change in dipole moment is expected. This is in agreement with similar findings for solvolysis of Pt(II) complexes,[24] where the solvent–substrate interaction is not of much kinetic significance because the nucleophilic discrimination factors change to approximately the same extent when the solvent is changed for various complexes. Our ΔV^* data, therefore, mainly reveal intrinsic effects in which the volume decrease associated with the binding of the entering solvent molecule is partially compensated for by the volume increase associated with the square-pyramidal to trigonal-bipyramidal transition as mentioned before. The partial molar volumes of the solvent molecules, as estimated from their densities at 20 °C, are 58.4 (EtOH), 40.4 (MeOH), 18.0 (H_2O), 70.9 (Me_2SO), 77.0 (DMF), and 52.2 $cm^3\ mol^{-1}$ (MeCN), from which it follows that there is no apparent correlation with the corresponding values of ΔV^*. Our earlier work has demonstrated that the extent of volume collapse during bond formation depends on the size of the entering solvent molecule, up to a point where this collapse is hindered by steric effects for large entering molecules.[12,25] It follows that this volume collapse could be very small in the case of a large molecule such as Me_2SO. The overall value of ΔV^* is therefore mainly controlled by steric and intrinsic effects. Finally, it should be mentioned that ΔV^* data of similar magnitude were reported for solvent exchange on $Pd(H_2O)_4^{2+}$ (−2.2 ± 0.2 $cm^3\ mol^{-1}$)[7] and for solvolysis of $Pd(H_2O)_3Me_2SO^{2+}$ (−1.7 ± 0.6 $cm^3\ mol^{-1}$),[26] which are both believed to occur according to an associative mechanism.

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Registry No. $Pd(Me_5dien)py^{2+}$, 117226-34-3; MeOH, 67-56-1; EtOH, 64-17-5; Me_2SO, 67-68-5; DMF, 68-12-2; MeCN, 75-05-8.

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ESR Studies of Intramolecular Electron Transfer in Malonic Acid Radical Chelates of Cerium(IV)

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The reduction of Ce(IV) complexed to dicarboxymethyl (malonic acid radical; $^{\bullet}CH(COOH)_2$) has been directly investigated by kinetic electron spin resonance spectrometry in aqueous perchloric acid media at 298 K. The corresponding first-order rate constant has a value of $k_{11} = (1.5 \pm 0.3) \times 10^3\ s^{-1}$. Free ($M_1$) and Ce(IV)-chelated ($M_2$) dicarboxymethyl radicals have slightly different magnetic parameters [$g(M_1) = 2.0039$, $a(H_\alpha)(M_1) = 20.3$ G, $g(M_2) = 2.0035$, $a(H_\alpha)(M_2) = 19.6$ G] and coexist in equilibrium, the ratio $r = [M_2]/[M_1]$ being a function of both [Ce(IV)] and $[H^+]$. The stability constant of the radical chelate, $K_8 = 242 \pm 31\ M^{-1}$, is considerably larger than that of malonic acid itself, $K_5 = 1.14\ M^{-1}$. The product $K_8 k_{11}$, which represents the overall rate constant for dicarboxymethyl radical oxidation by Ce(IV), has a value within the range of those measured for the direct oxidations of substituted secondary alkyl radicals by Ce(IV), Co(III), and Ti(IV).

Introduction

Electron-transfer reactions between transition metal cations and alkyl radicals is an area of current interest.[1-5] They are relatively fast processes with rate constants in the range 10^5–$10^6\ M^{-1}\ s^{-1}$ and can proceed in principle either by a direct mechanism or by

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