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Volumes of Activation for the Solvolysis of $[Pd(Et_4dien)I]^+$ in Different Solvents

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The pressure dependencies of the rates of solvolysis of $[Pd(Et_4dien)I]^+$ *in the presence of 0.05* M Br^- *were measured in methanol, ethanol, dimethyl sulfoxide, N,N-dimethylformamide and acetonitrile at 40 °C. The respective volumes of activation are* -13.4 ± 0.5, -12.9 ± 0.4, -10.1 ± 0.2, -9.3 ± 0.3 *and* -7.9 ± 0.5 cm^3 mol^{-1}. *The temperature dependencies of the rate constants were also determined for the solvents acetonitrile, acetone and N,N-dimethylacetamide to supplement the existing data in the remaining solvents. An associative interchange mechanism is favored to explain these results.*

Introduction

The reaction sequence for the solvolysis step in the substitution reactions of the so-called 'pseudo octahedral' complexes containing the ligand 'Et_4dien' [1] is as follows:

$$[Pd(Et_4dien)X]^+ + S \xrightarrow{k_1} [Pd(Et_4dien)S]^{2+} + X^- \quad (1)$$

$$[Pd(Et_4dien)S]^{2+} + Y^- \xrightarrow{fast} [Pd(Et_4dien)Y]^+ + S \quad (2)$$

The hydrolysis step (*i.e.* S = H_2O) is generally thought to involve an I_a mechanism [2–6]. A recent high pressure investigation [7] of these reactions in our laboratory also confirmed the assignment of a basically associative mechanism. From these results we were able to construct a volume profile of equation (1) and thereby assess the magnitudes of the contributions to the volume of activation, $\Delta V^{\neq}_{exp}$, stemming from Pd–OH_2 bond formation and Pd–X bond stretching. The former was considered to be virtually complete in the transition state and involved a decrease in volume of *ca.* 16 cm^3 mol^{-1}, whereas Pd–X bond dissociation was assumed to be only 50% complete with respect to the volume change accompanying total cleavage of this bond. The dissociative contribution is a function of the size, charge and specific solvation characteristics of the leaving group.

The substitution reactions of $[Pd(Et_4dien)Br]^+$ have been studied in the solvents CH_3OH, DMSO and CH_3CN [8]. The solvolysis rate constants k_1 decrease in the order H_2O [2, 3] > DMSO > CH_3OH > CH_3CN. Thus, whereas for nonsterically restricted systems such as the $^{36}Cl^-$ exchange in *trans*-$[Pt(py)_2Cl_2]$, $k_1(DMSO) = 108\ k_1(H_2O)$ [9], here $k_1(H_2O) = 25\ k_1(DMSO)$. It was argued [8] that in the former case the greater affinity of Pt(II), and to a lesser extent Pd(II), to soft Lewis bases accounts for the enhanced reactivity of DMSO through Pt–S bond formation. However, the bulkier DMSO has more difficulty than the smaller H_2O in approaching the crowded Pd(II) center. Specific solvation of the ethyl group of Et_4dien was also invoked in order to rationalize the appearance of a nucleophile-dependent reaction pathway for Y = Cl^- and I^- which was absent in the remaining solvents [8].

Roulet and Gray [4] carried these arguments a step further following their investigation of the kinetics of the substitution by Y^- in $[Pd(Et_4dien)X]^+$, where X and Y = Cl^-, Br^- or I^-, in the solvents CH_3OH, C_2H_5OH, i-C_3H_7OH, H_2O, DMSO and DMF. They concluded that these solvolysis reactions are associative in protic solvents, but are dissociative in DMSO and DMF. The somewhat less negative $\Delta S^{\neq}$ values found for DMSO and DMF were considered as evidence of this discontinuity of mechanism.

Experimental

$[Pd(Et_4dien)I]I$ was prepared and recrystallized by the method of Baddley and Basolo [2]. It was converted to the perchlorate salt by adding a large excess of $LiClO_4$ to a filtered aqueous solution of the iodide salt. The resulting yellow precipitate was filtered off, then washed with a minimum amount of ice-cold water and dried at 60 °C. The perchlorate salt proved to be much more soluble in the solvents chosen here.

The solvents methanol, ethanol, DMSO, DMF, DMA and acetonitrile were purified and dried by standard procedures [10]. Spectroscopic grade acetone was used without further purification. Bromide ion was added in the form of dried LiBr or $(C_4H_9)_4NBr$.

TABLE I. First-order Rate Constants for the Solvolysis of $[Pd(Et_4dien)I]^+$ in Various Solvents as a Function of Pressure at 40 °C and $\mu \approx 0.05$ *M* = $[Br^-]$.

Solvent	10^4 k_1[a] (s^{-1}) Pressure (bar)						
	1	250	500	750	1000	1250	1500
Methanol	0.342	0.413	0.453	0.537	0.609	0.661	0.765
Ethanol	0.153	0.171	0.194	0.210	0.248	0.286	0.322
DMSO	4.04	4.44	4.84	5.46	6.00	6.72	7.19
DMF	1.93	2.20	2.34	2.53	2.87	3.11	3.35
Acetonitrile	1.19	1.33	1.41	1.43	1.64	1.77	1.92

[a] Average error is *ca.* ±2%.

TABLE II. First-order Rate Constants for the Solvolysis of $[Pd(Et_4dien)I]^+$ in Various Solvents as a Function of Temperature at $\mu \approx 0.05$ *M*.

Acetonitrile		Acetone		DMA	
T (°C)	10^4 k_1 (s^{-1})	T (°C)	10^4 k_1 (s^{-1})	T (°C)	10^4 k_1 (s^{-1})
29.5	0.462	30.5	0.553	28.7	0.556
34.6	0.640	34.9	0.882	35.1	1.19
40.0	1.19	40.0	1.56	40.0	1.91
44.6	1.86	45.1	2.76	44.9	3.21
52.2	3.88	49.1	4.05	50.1	5.21

The reaction rates were measured spectrophotometrically on a Cary 15 instrument equipped with a thermostatted (±0.1 °C) high pressure cell [11]. A flanged teflon/quartz cuvette [11] was seated inside the pressure vessel. Although this arrangement proved to be highly satisfactory for most solvents, DMA and acetone were found to affect the O-rings used to seal the cuvette with the result that the rate constants obtained in these particular solvents under pressure were irreproducible. The change in absorbance was monitored at either 305 or 430 nm.

Results

The rate constants for the overall reaction,

$$[Pd(Et_4dien)I]^+ + Br^- \rightarrow [Pd(Et_4dien)Br]^+ + I^- \quad (3)$$

were found to be independent of the $[Br^-]$ *viz.* $\leqslant 0.05$ *M*. This reaction also proceeds to completion under these conditions [8]. The first-order rate constants, which are listed in Table I as a function of pressure up to 1.5 kbar, are the average values of at least two individual experiments. Plots of $\ln k_1$ *versus* pressure were linear within experimental error, as was also found for the analogous reactions in aqueous solutions [7]. Therefore, the $\Delta V^{\neq}_{exp}$'s were derived from a linear least-squares analysis of these data.

The temperature dependence of k_1 was studied for the solvents, acetonitrile, DMA and acetone, to supplement the existing data [4, 6] (Table II).

The combined rate constants at atmospheric pressure and corresponding activation parameters are given in Table III.

Discussion

The rate constants in Table III exhibit a clear trend in the three protic solvents, whereas they remain relatively constant in the aprotic solvents investigated. This trend amounts to a factor of *ca.* 100 and apparently originates solely from an increase in $\Delta H^{\neq}$, which in turn can be assigned to a decrease in the nucleophilicity of the incomming solvent molecule. By comparison, other factors such as the size of the solvent molecule and solvation of the leaving iodide ligand seem to be minor considerations in determining the rate of solvolysis in these three protic solvents as $\Delta S^{\neq}$ remains constant within experimental error.

The most surprising aspect of all the k_1 and $\Delta H^{\neq}$ values is their consistency despite the varied nature of the solvents listed here, *cf.* the dielectric constants for C_2H_5OH, CH_3OH, H_2O, $(CH_3)_2SO$, $(CH_3)_2NCHO$, CH_3CN, $(CH_3)_2CO$ and $(CH_3)_2NC(CH_3)O$ are 24.55, 32.7, 78.54, 46.68, 36.71, 37.5, 20.7 and 37.78, respectively. This insensitivity of k_1 must be further stressed since we are dealing with solvolysis reactions where the solvent plays both a direct and an indirect (solvation) role. Taking into account the error limites of the $\Delta S^{\neq}$ values, they exhibit only minor fluctuations so that it is difficult to accept the concept [4] that a change in mechanism to a basically dissociative mode is involved in the 'bulkier' dipolar aprotic solvents, *e.g.* DMSO, DMF and DMA. We therefore prefer to consider that a common pro-

TABLE III. Activation Parameters for the Solvolysis of $[Pd(Et_4dien)I]^+$ at $[Br^-] = 0.05\ M \cong \mu$ and at 40 °C.

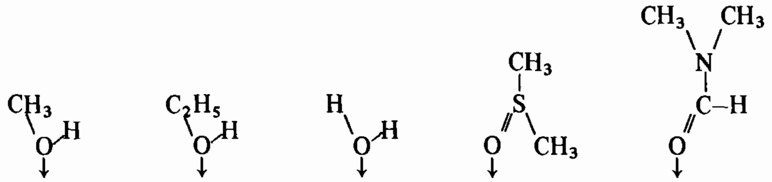
Solvent	$10^4\ k_1$ (s^{-1})	$\Delta V^{\neq}_{exp}$ ($cm^3\ mol^{-1}$)	$\Delta H^{\neq}$ ($kJ\ mol^{-1}$)	$\Delta S^{\neq}$ ($J\ K^{-1}\ mol^{-1}$)
C_2H_5OH	0.153	−12.9 ± 0.4	85.3 ± 2.1^{a}	−67 ± 8^{a}
CH_3OH	0.342	−13.4 ± 0.5	83.2 ± 2.1^{a}	−63 ± 8^{a}
H_2O	14.1^{b}	−11.5 ± 0.2^{b}	76.9 ± 2.1^{a}	−55 ± 8^{a}
	14.0^{c}		71.4 ± 1.3^{c}	−69 ± 3^{c}
$(CH_3)_2SO$	4.04	−10.1 ± 0.2	81.9 ± 2.1^{a,d}	−42 ± 8^{a,d}
$(CH_3)_2NCHO$	1.93	−9.3 ± 0.3	81.5 ± 2.1^{a,d}	−46 ± 8^{a,d}
CH_3CN	1.19	−7.9 ± 0.5	76.0 ± 3.8	−78 ± 12
$(CH_3)_2CO$	1.56		85.4 ± 1.0	−45 ± 3
$(CH_3)_2NC(CH_3)O$	1.88		81.5 ± 1.2	−55 ± 4

[a] Recalculated from the data in ref. 4. [b] Ref. 7. [c] Ref. 6. [d] Cl^- was the nucleophile used in this case, however this has no influence on the rates or activation parameters.

cess is involved, namely Pd–O bond formation, with the obvious exception of acetonitrile. Although, even in this apparent exception the similarity of the 'hard' N of CH_3CN to the oxygens of the remaining solvents is reflected in the virtually identical rate parameters. The equality of the rate data in DMSO and acetone is particularly significant. It leads to the conclusion that the ambidentate DMSO molecule, when placed under the steric restrictions imposed by the ethyl groups of the Et_4dien ligand, is capable of bonding through the normally less energetically favored O atom. This accounts for the reduced reactivity of DMSO relative to water in these substrates.

The mode of activation in all the solvents listed in Table III is, therefore, postulated to involve a basically associative solvolysis process. As an earlier detailed high pressure study [7] of these reactions in aqueous solution was able to confirm the mechanism to be of the I_a type [5], this may be taken as the prevailing mechanism in these solvents.

Attention can now be focussed on the $\Delta V^{\neq}_{exp}$ values given in Table III. Supporting volume data – partial molar volumes of the reacting species or the total volume change – such as were utilized in studies of aqueous solutions are not obtainable in these solvents. For example, a reliable and above all, accurate method of separating partial molar volumes into their constituent ionic components is not as yet fully developed [12]. Consequently, a precise quantitative appraisal of the $\Delta V^{\neq}_{exp}$ on the basis of a total volume profile is not possible at the present time. Nevertheless, the absolute values of $\Delta V^{\neq}_{exp}$ show a definite trend in the order $CH_3OH \sim C_2H_5OH > H_2O > (CH_3)_2SO > (CH_3)_2NCHO$, which parallels the order of decreasing cross-sectional area at the oxygen atom of these solvent molecules and is in turn directly related to the volume swept out by the solvent molecule during bond formation. This can be more clearly shown by the following schematic representations:



The cross-section must then be taken in close proximity to the coordinating oxygen as this represents the limit of penetration into the first coordination sphere or, in other words, this corresponds to the volume decrease in the system resulting from the partial insertion of the solvent molecule into the coordination sphere. The linear CH_3CN molecule, with its inherently smaller cross-sectional area would, consequently, also be expected to give the smallest $\Delta V^{\neq}_{exp}$ in this series and this was indeed found to be the case. Partial bonding of at least one solvent molecule to the Pd(II) center may occur in the initial state, but this would not affect the arguments brought here. Moreover, the established existence of five-coordinate forms of $[Co(Et_4dien)Cl_2]$ [13] and $[Ni(Et_4dien)Cl_2]$ [14] show that not only should it be possible to have weak interaction between the larger Pd(II) center and a solvent molecule, but this molecule should be able to enter the first coordination sphere during the activation step, especially when the I ligand is believed to be 50% dissociated.

The partial dissociation of the iodide ligand must be associated with a intrinsic volume increase which, however, will be the same in each solvent. In addition, dissociation must result in some charge separation thereby causing an increase in electrostriction and a resulting negative contribution to $\Delta V^{\neq}_{exp}$. We can only conclude that in the solvents investigated under pressure, they are so well structured that the introduction of partial charges causes a small and, therefore, similar degree of electrostriction in each solvent, such that maximum differences in volume of 1 to 2 $cm^3 mol^{-1}$ arise [15]. In this respect it is particularly relevant that for the solvolysis of Pd(Et_4-dien)I^+ in water a $\Delta V^{\neq}_D$ of +4.8 $cm^3 mol^{-1}$ was assigned to the 50% dissociation of iodide in the transition state [7]. The positive sign established that the intrinsic volume change exceeds the solvation contribution so that it can be assumed that the latter is relatively small and therefore does not significantly affect the sequence of the $\Delta V^{\neq}_{exp}$ values. This is in agreement with the explanation of the relative magnitudes of the k_1 values given earlier in the discussion.

In conclusion, the kinetic data presented in this publication are considered as strong evidence for an associative solvolysis mechanism of the I_a type prevailing in the substitution reactions of [Pd(Et_4-dien)X]$^{n+}$ complexes in different solvents.

Acknowledgments

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References

1 Et_4 dien = 1,1,7,7-tetraethyldiethylenetriamine. Other abbreviations have also been used, *viz.* IEDA ≡ iminobis(ethylenediethylamine) and TEDEN ≡ N'-[2-(diethylamino)ethyl]-N,N-diethylethane-1,2-diamine.
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15 It is important to remember that the largest volume changes are found in the nonpolar solvents which, by definition,are the most poorly structured ones.