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Volumes of Activation for the Anation of Pd(II) Substituted Dien Complexes by Chloride Ion in Aqueous Solution. A High Pressure Stopped-Flow Instrument for Studying the Kinetics of Fast Reactions under Pressure

R. VAN ELDIK*, D. A. PALMER**, R. SCHMIDT and H. KELM*

Institute for Physical Chemistry, University of Frankfurt, Robert Mayer Str. 11, 6000 Frankfurt am Main, F.R.G.

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The kinetics of anation of Pd(1,1,7,7-Et$_4$dien)-OH$_2^{2+}$ and Pd(1,1,4-Et$_3$dien)OH$_2^{2+}$ by chloride ion were studied under pressures up to 1 kbar using a high pressure stopped-flow system. The construction and testing of the latter system are discussed in detail. The rate and activation parameters for the above reactions are: k(25 °C) = 4.2 ± 0.1 and 1558 ± 68 M^{-1} *sec*$^{-1}$*;* $\Delta H^{\neq} = 13.4 \pm 0.4$ *and 10.5 ± 0.7 kcal mol*$^{-1}$*;* $\Delta S^{\neq} = -10.7 \pm 1.2$ *and −8.7 ± 2.3 cal K*$^{-1}$ *mol*$^{-1}$*; and* $\Delta V^{\neq} = -3.0 \pm 0.2$ *and −2.7 ± 0.2 cm*^{3} *mol*$^{-1}$*, respectively. These are considered as evidence for an associative type of anation process.*

Introduction

Substitution reactions of square planar complexes of the type

$$ML_3X + Y \rightarrow ML_3Y + X$$

usually proceed according to the well-known two term rate law [1, 2] with

$$k_{obs} = k_1 + k_2[Y]$$

The k_2-term represents the direct associative attack of the nucleophile Y, whereas the k_1-term represents the solvolysis path in which a solvent-containing intermediate ML_3S is formed and subsequently undergoes a rapid substitution (anation when S = H_2O) reaction to produce the final product.

In an earlier study [3] we investigated the pressure dependence of such an anation process, *viz.* the anation of Pd(4-Me-1,1,7,7-Et$_4$dien)OH$_2^{2+}$ by chloride ion. Since this is only a moderately fast reaction, the rate being largely reduced by the steric crowding on the dien ligand [4–7], a special mixing system was constructed which enabled the study of reactions with half-lives of 10 seconds or longer under pressure. In order to investigate other anation reactions in this series, we constructed a high pressure stopped-flow system which enables the study of reactions with half-lives ⩾ 20 msec. A description of this instrument, as well as high pressure kinetic data for the anation reactions of Pd(1,1,7,7-Et$_4$dien)OH$_2^{2+}$ and Pd(1,1,4-Et$_3$dien)OH$_2^{2+}$ are presented in this paper.

Experimental

Description of the High Pressure Stopped-Flow System

The instrument was basically constructed following the suggestions of Heremans *et al.* [8] with some modifications in the syringes employed. A schematic drawing of the instrument along with details on the construction of the mixing chamber and syringes, is presented in Fig. 1. A two-ring sealing system is used in the syringes and the outer ring is made out of a low friction resistance material. The tightness of the syringe seal can be set with the adjustable piston plate. The mixing cell and syringes are constructed from a polyamid material, *viz.* Kel-F. The movement of the drive plate during activation of the single-step motor is assisted by two springs located between the drive and base plates. During the assembly procedure the receiver syringe is filled with the appropriate solvent and used to flush the mixing cell. The reagent syringes are then filled and placed onto the mixing cell. The entire stopped-flow device is inserted into a thermostatted (±0.1 °C) high pressure cell, filled with n-heptane as pressurizing medium. The optical base line of the spectrometer is adjusted while the mixing cell is filled with solvent, prior to mixing. An overall view of the complete instrumental arrangement is presented in Fig. 2. Light carriers are used to transmit the light through the high pressure cell, making the system easily inter-

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*Authors to whom correspondence should be addressed.

**Present address: Chemistry Division, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tenn. 37830, USA.

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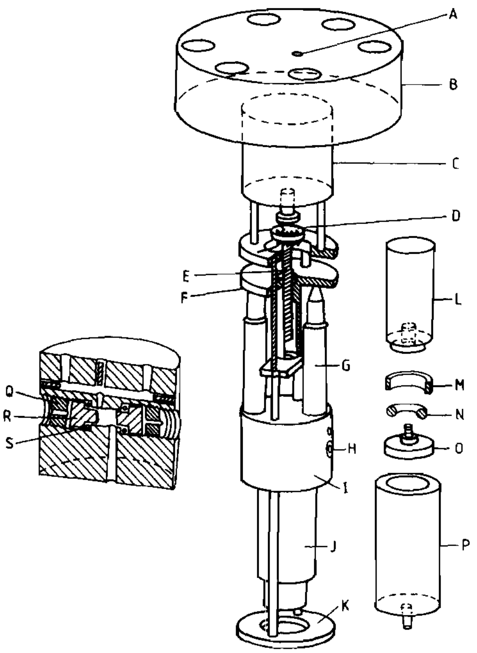

Fig. 1. Schematic drawing of high pressure stopped-flow instrument

A – Electrical feed through
B – Pressure vessel lid
C – Single-step motor (Kuhnke D 39-32 ROR)
D – Gear mechanism
E – 'Cork screw' action
F – Driving plate
G – Reagent syringe
H – Optical window
I – Mixing cell
J – Receiver syringe
K – Base plate
L – Piston
M – Outer bronze/PTFE ring
N – Inner Viton ring
O – Adjustable piston plate
P – Syringe body
Q – Metal screw
R – Quartz window
S – Viton ring

changeable with a normal pressure stopped-flow unit. In the present study an Aminco light source, monochromator and data acquisition/storage system was used.

The performance of the system was tested using the Fe^{3+}/NCS^- system. The results, summarized in Table I, demonstrate that a pressure independent average mixing time of ca. 20 msec can be obtained for pressures up to 1000 bar.

Kinetic Measurements

The complexes $[Pd(1,1,7,7\text{-}Et_4dien)Br]ClO_4$, $[Pd(1,1,4\text{-}Et_3dien)Cl]ClO_4$ and $[Pd(dien)Cl]ClO_4$ were prepared according to standard procedures [4, 5]. Chemical analyses were in good agreement with the theoretical values. The corresponding aquo complexes, $PdL_3(OH_2)^{2+}$, were prepared in solution by treating the above complexes with an equivalent quantity of $AgClO_4$ at 60 °C, followed by cooling, filtering, diluting the filtrate to a known volume and adjusting the pH of the final solution to 3. UV-visible absorption spectra, recorded on a Perkin Elmer 555 spectrophotometer, are in good agreement with those reported before [4, 5, 9]. The absorption maxima of the halogeno and aquo complexes in the range 300 to 400 nm move to longer wavelengths and higher intensity with increase in steric crowding on the dien ligand. The halogeno complexes absorb more weakly and at approx. 20 nm longer wavelengths than the corresponding aquo complexes, with the result that the anation reactions can be studied conveniently in the range 300 to 320 nm.

TABLE I. Determination of Mixing Time of High Pressure Stopped-Flow System:

$Fe^{3+} + NCS^- \longrightarrow FeNCS^{2+}$

$[Fe^{3+}] = 5 \times 10^{-3} M$, $[NCS^-] = 1 \times 10^{-2} M$,

$[H^+] = 1 \times 10^{-2} M$, Temp. = 25 °C, wavelength = 460 nm.

Pressure bar	Mixing time msec				Average msec
25	19	20	18	19	19.0
200	21	21	20	20	20.5
400	19	21	20	21	20.3
600	18	18	20	19	18.8
800	17	17	18	17	17.3
1000	20	18	19	20	19.3

Doubly distilled water and chemicals of analytical reagent grade were used in preparing all solutions. The pH was adjusted with $HClO_4$, whereas the ionic strength was controlled with $NaClO_4$. Concentrations quoted are those obtained after mixing. Pseudo-first-order plots of $\ln(A_t - A_\infty)$ *versus* t, where A_t and A_∞ are the absorbances at time t and infinity, respectively, were linear for at least three to four half-lives. The observed rate constants were calculated in the usual way and the reported values represent the mean of four to eight kinetic runs.

Results and Discussion

In an earlier study the pK of $Pd(Et_4dien)OH_2^{2+}$ was determined spectrophotometrically and was reported [9] to be 7.50 ± 0.08 at 20 °C. A similar determination was repeated for the $Pd(Et_3dien)OH_2^{2+}$ complex, and a pK value of 6.55 ± 0.05 at 25 °C was found. These values are such that at pH ~ 3 the only species in solution are the aquo complexes. The conjugate base forms, *i.e.* hydroxo species, are therefore not considered to be of any significance.

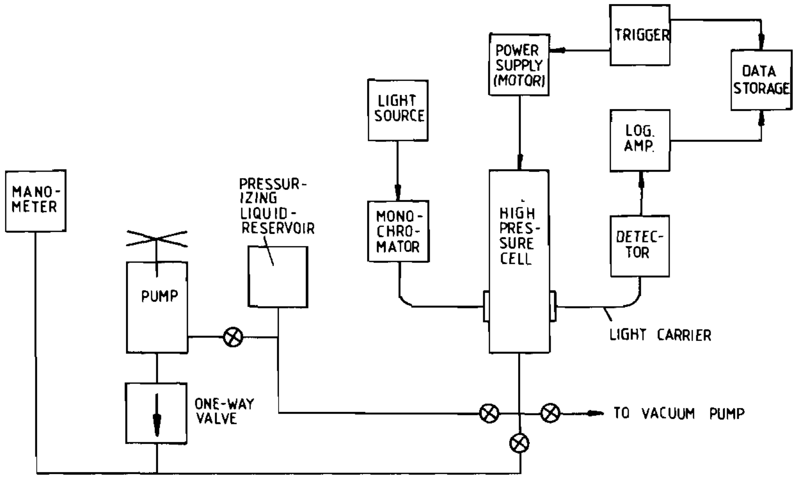

Fig. 2. Schematic diagram of overall set up.

TABLE II. Rate Data for the Anation of $Pd(Et_4dien)OH_2^{2+}$ by Cl^-: $[Pd(II)] = 1 \times 10^{-3}$ *M*, $[H^+] = 1 \times 10^{-3}$ *M*, ionic strength = 0.1 *M*, wavelength = 320 nm.

Temp. °C	Pressure bar	k M^{-1} sec^{-1}	k′ M^{-1} sec^{-1}	Activation Parameter
7.7	1	1.02 ± 0.01		$\Delta H^{\neq} = 13.4 \pm 0.4$ kcal mol^{-1}
16.0		2.17 ± 0.03		
25.0		4.19 ± 0.06		$\Delta S^{\neq} = -10.7 \pm 1.2$ cal K^{-1} mol^{-1}
34.2		9.10 ± 0.13		
25.0	10	4.25 ± 0.09	4.25 ± 0.09	$\Delta V^{\neq} = -3.0 \pm 0.2$ cm^3 mol^{-1}
	250	4.40 ± 0.04	4.35 ± 0.04	
	500	4.62 ± 0.07	4.53 ± 0.07	
	750	4.75 ± 0.05	4.61 ± 0.11	
	1000	5.00 ± 0.05	4.81 ± 0.05	

In some preliminary experiments at normal pressure it was observed that the pseudo-first-order rate constant for the anation of $Pd(Et_4dien)OH_2^{2+}$ and $Pd(Et_3dien)OH_2^{2+}$ by chloride ion, depends linearly on the chloride ion concentration. This is within expectation and in agreement with similar observations reported elsewhere [3, 5, 7], but contradicts earlier data reported [10] for the anation reactions of $Pt(dien)OH_2^{2+}$. The anation of $Pd(dien)OH_2^{2+}$ by Cl^- was found to occur within the mixing time of the stopped-flow instrument such that no reliable rate data could be recorded for this fast reaction.

The rate constants as a function of temperature and pressure for the anation of $Pd(Et_4dien)OH_2^{2+}$ and $Pd(Et_3dien)OH_2^{2+}$ by Cl^- are reported in Tables II and III, respectively. The second-order rate constant (k) was calculated from the expression

$$k_{obs} = k[Cl^-]$$

and its values at elevated pressures were corrected (k′) for the compressibility of the solvent [11]. The volume of activation ($\Delta V^{\neq}$) was calculated in the usual way from the slope of the plot of ln k′ versus p, which was found to be linear in both cases within experimental error limits.

The results in Tables II and III illustrate that the reproducibility of the high pressure stopped-flow system (data at $p \geqslant 10$ bar) is of the same order as that of the normal pressure system (data at $p = 1$ bar). Even for half-lives of *ca.* 40 msec, *i.e.* the anation of $Pd(Et_3dien)OH_2^{2+}$ at $[Cl^-] = 1 \times 10^{-2}$ *M*, the standard deviation being 2 to 4% for pressures up to 1000 bar. The resulting values for $\Delta V^{\neq}$, although rather small, show very low standard deviations compared to those normally found in high pressure studies, and further underline the sensitivity and reproducibility of the system.

The rate parameters for anation reactions of different Pd(II) dien complexes are summarized in Table IV. First of all it is very obvious that k increases significantly on decreasing the steric hindrance on the dien ligand. This tendency, and the

TABLE III. Rate Data for the Anation of $Pd(Et_3dien)OH_2^{2+}$ by Cl^-: $[Pd(II)] = 1 \times 10^{-3}$ *M*, $[H^+] = 1 \times 10^{-3}$ *M*, ionic strength = 0.1 *M*, wavelength = 320 nm.

Temp. °C	Pressure bar	k M^{-1} sec^{-1}	k′ M^{-1} sec^{-1}	Activation Parameter
7.7	1	475 ± 7		$\Delta H^{\neq}$ = 10.5 ± 0.7 kcal mol^{-1}
16.0		751 ± 35		
25.0		1558 ± 68		$\Delta S^{\neq}$ = −8.7 ± 2.3 cal K^{-1} mol^{-1}
34.2		2525 ± 87		
25.0	10	1515 ± 26	1515 ± 26	$\Delta V^{\neq}$ = −2.7 ± 0.2 cm^3 mol^{-1}
	250	1576 ± 61	1558 ± 60	
	500	1640 ± 41	1606 ± 40	
	750	1709 ± 35	1657 ± 34	
	1000	1751 ± 74	1684 ± 71	

TABLE IV. Rate Parameters for the Reaction $PdL_3OH_2^{2+} + Cl^- \longrightarrow PdL_3Cl^+ + H_2O$.

L_3	4-Me-1,1,7,7-Et$_4$dien[a]	1,1,7,7-Et$_4$dien	1,1,4-Et$_3$dien
k at 25 °C, M^{-1} sec^{-1}	2.27 ± 0.01	4.19 ± 0.06	1558 ± 6.8
$\Delta H^{\neq}$, kcal mol^{-1}	16.8 ± 0.4	13.4 ± 0.4	10.5 ± 0.7
$\Delta S^{\neq}$, cal K^{-1} mol^{-1}	−0.3 ± 1.3	−10.7 ± 1.2	−8.7 ± 2.3
$\Delta V^{\neq}$, cm^3 mol^{-1}	−7.7 ± 0.5	−3.0 ± 0.2	−2.7 ± 0.2

[a] Data taken from ref. 3.

normal pressure values of k are in good agreement with that reported elsewhere [4, 5, 7]. The drastic increase in k for the last entry (1,1,4-Et$_3$dien) illustrates the effect of removing the steric restraints imposed by the 7th position of the dien ligand on the *cis*-aquo ligand. The associative nature of the reaction mechanism is emphasized by this tendency. Furthermore, the trend in the values of $\Delta H^{\neq}$ confirm this conclusion since $\Delta H^{\neq}$ decreases with decreasing steric crowding. The $\Delta H^{\neq}$ values are very typical of substitution reactions of Pd(II) and Pt(II) dien complexes [9, 12–15].

The $\Delta S^{\neq}$ values in Table IV are only slightly negative and therefore deviate from the general empirical observation that reactions of Pt(II) and Pd(II) exhibit strongly negative entropies of activation attributable to an associative process. However, it appears to be significant that they do not parallel the values of $\Delta V^{\neq}$ as inferred previously [16]. Certainly the better accuracy of the latter allow us to be more confident as to the reality of the trends in them.

Le Noble *et al.* [17] have indicated that $\Delta V^{\neq}_{intr}$, which represents the contribution to $\Delta V^{\neq}$ arising from alterations in bond lengths and angles during the formation of the transition state [18–20], becomes more negative for sterically hindered associative reactions. It was suggested that this effect is a manifestation of the Hammond postulate [21]. Accordingly, sterically hindered reactions will have a later, or more product-like, transition state. This may explain the more negative $\Delta V^{\neq}$ value for the anation of the most sterically crowded complex, $Pd(MeEt_4dien)OH_2^{2+}$, compared to the remaining two complexes listed in Table IV. However, this concept overlooks the second, and often dominant, contribution to $\Delta V^{\neq}$, namely $\Delta V^{\neq}_{solv}$ which reflects variations in solvation [18–20]. This may be important in the case of $Pd(Et_3dien)OH_2^{2+}$, due to the presence of the protic amine cis to the aquo ligand.

A recent study [15] of the hydrolysis of a series of $Pd(Et_4dien)X^{n+}$ complexes, where X = Cl, Br, N_3, I, NCS and NH_3, established the reaction mechanism to be of the interchange type with the high pressure data favouring an I_a mechanism. By the principle of microscopic reversibility, the anation of $Pd(Et_4dien)OH_2^{2+}$ must also conform to an I_a mechanism. A mechanism of this type involves a positive $\Delta V^{\neq}_{intr}$ due to stretching of the $Pd-OH_2$ bond with virtually no conceivable effects of $\Delta V^{\neq}_{solv}$, unless specific solvation effects are operative as eluded to in the previous paragraph. On the other hand, Pd–Cl bond formation results in a negative $\Delta V^{\neq}_{intr}$ with a concomitant positive $\Delta V^{\neq}_{solv}$ due to partial charge neutralization. Therefore it must be concluded that bond formation is the dominant contribution to the observed negative $\Delta V^{\neq}$. It should be noted that $\Delta V^{\neq}$ for the hydrolysis of $Pd(Et_4dien)Cl^+$ is substantially more negative (*viz.*

-14.9 ± 0.2 cm^3 mol^{-1}) [15] than for the reverse reaction. In this case, $\Delta V^{\neq}_{\text{solv}}$ is negative thereby reinforcing $\Delta V^{\neq}_{\text{intr}}$ for bond formation.

The volume change for the overall hydrolysis reaction, $\Delta\bar{V}$, can be readily calculated from the two complementary $\Delta V^{\neq}$ values. For the Pd(Et$_4$dien)Cl$^+$ hydrolysis/anation equilibrium $\Delta\bar{V} = -14.9 - (-3.0) = -11.9 \pm 0.4$ cm^3 mol^{-1}, whereas for the corresponding Pd(MeEt$_4$dien)Cl$^+$ system $\Delta\bar{V} = -17.5 - (-7.7) = -9.8 \pm 0.8$ cm^3 mol^{-1}. In both cases the transition state is smaller in volume than either of the initial states, providing further evidence for an associative process. Furthermore, using the known partial molar volume of Pd(Et$_4$dien)Cl$^+$ (245.8 ± 0.8 cm^3 mol^{-1}) [17] and Cl$^-$ (21.8 cm^3 mol^{-1}), $\bar{V}$(Pd(Et$_4$dien)OH$_2^{2+}$) can be calculated to be 230.1 ± 1.2 cm^3 mol^{-1}. This is in reasonable agreement with predicted values between 228 ± 2 and 225 ± 2 cm^3 mol^{-1} [3]. It should also be emphasized that in the earlier publication [15] on the hydrolysis reactions of Pd(Et$_4$dien)X^{n+} complexes, in the absence of a value for $\bar{V}$(Pd(Et$_4$dien)OH$_2^{2+}$), it was assumed that it was equal to $\bar{V}$(Pd(Et$_4$dien)NH$_3^{2+}$) $= 225 \pm 0.7$ cm^3 mol^{-1} for the purpose of estimating the $\Delta\bar{V}$ values for the series of Pd(Et$_4$dien)X^{n+} hydrolysis reactions. This discrepancy of 5 cm^3 mol^{-1} does not affect one of the arguments used to establish an I$_a$ mechanism because this was based on the slope of the $\Delta V^{\neq}$ versus $\Delta\bar{V}$ plot, and is therefore independent of the absolute value of $\Delta\bar{V}$.

Unfortunately, no volume data are available on the hydrolysis reaction of Pd(Et$_3$dien)Cl$^+$. However, it is our intention to investigate a wider range of these complexes with various degrees of steric crowding. In particular, it would be interesting to establish whether the reaction mechanism reverts to the A type in the absence of substantial steric hindrance. One can speculate that the Pd(Et$_3$dien)Cl$^+$ system may even approach the limiting A mechanism as this would reduce the positive contribution to $\Delta V^{\neq}$ for the anation of the aquo analogue for reasons cited above, which in turn would modify the trend in $\Delta V^{\neq}$ as expected from le Noble's hypothesis [17] for the effect of steric hindrance on $\Delta V^{\neq}$. Preliminary results on the hydrolysis of Pd(Et$_3$dien)Cl$^+$ indeed show that $\Delta S^{\neq}$ is remarkably more negative than those reported [15] for the hydrolysis of Pd(Et$_4$dien)X$^+$ (X = Cl, Br, I, N$_3$, NCS), which is in line with the above arguments for a limiting A mechanism.

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