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A Reinvestigation of the Pressure Dependence of the Rate of Hydrolysis of Pt(dien)X$^+$ Complexes

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The pressure dependencies of the first-order rate constants for the hydrolysis of Pt(dien)Br$^+$ with Br$^-$ and ClO$_4^-$ as counter ions were measured at 25 °C, both in the absence of added 'inert' electrolyte and in 0.2 M *solutions of LiClO$_4$, NaClO$_4$ and NaBr. A similar study of the hydrolysis of [Pt(dien)Cl] Cl was also carried out at NaClO$_4$ concentrations of 0, 0.2 and 1.0 M. In all cases the logarithm of the rate constant was a* linear *function of pressure up to the maximum pressure applied of 1.75 kbar. The volume of activation, $\Delta V_1^{\neq}$, varied between –9.0 and –10.5 cm^3 mol^{-1}.*

Introduction

The hydrolysis of Pt(dien)X$^+$ complexes can be represented by the equation [1],

$$\mathrm{Pt(dien)X^+ + H_2O \rightleftharpoons Pt(dien)OH_2^{2+} + X^-}$$

such that in basic solution the rapid deprotonation of the aqua ligand stabilizes the otherwise kinetically unstable product [2]. Consequently, the rate of hydrolysis is independent of [OH$^-$].

Several years ago we investigated the pressure dependence of the reaction in which X = Br$^-$ – the substitution reactions were also studied – and we observed a marked pressure dependence of the volume of activation, $\Delta V_1^{\neq}$ [3]. The dependence was so acute, particularly at lower pressures (1–500 bar), that it was difficult to obtain a reliable value for $\Delta V_1^{\neq}$ at atmospheric pressure, although a value of –18 ± 2 cm^3 mol^{-1} was reported. Not only were the mechanistic implications of this phenomenon of importance, but also the physical origin of such pressure dependencies ($\Delta\beta_1^{\neq}$) is of general interest. We therefore undertook to study this particular reaction in more detail with the aim of looking at the ionic strength dependence of $\Delta V_1^{\neq}$ and $\Delta\beta_1^{\neq}$ as we believe that $\Delta\beta^{\neq}$, which stems from solvation effects, should become less significant in the presence of structure-breaking electrolytes [4]. However, in this work curvature of the ln k$_1$ *versus* pressure plots could not be detected, despite the fact that a variety of electrolytic solutions were investigated. These findings are now reported in the following text.

Experimental

[Pt(dien)Br] Br and [Pt(dien)Cl] Cl were prepared using a modified version [3] of the method of Mann [5]. The former complex was converted to the perchlorate salt by dissolving it in a minimum amount of water at 60 °C and filtering the hot solution onto solid LiClO$_4$. After cooling to room temperature, the precipitate was filtered off and washed with ethanol, then dried at 80 °C.

Doubly distilled water was used in all the kinetic work.

The reactions were followed *in situ* on a converted Zeiss PMQ II spectrophotometer equipped with a beam-splitter to monitor the 'incident light' The high pressure vessel and associated equipment have been described elsewhere [6]. A recently developed cylindrical quartz cuvette [7] was used and proved to be highly suited to studying reactions in aqueous solution. The cuvette has an effective path length of *ca.* 1.5 cm which enhanced the large absorbance change associated with these reactions, thereby resulting in very accurate rate measurements. The reactions of the respective bromo and chloro complexes were monitored at 280 and 240 nm.

Results

The rate constants were calculated in the usual manner from plots of ln (A$_\infty$ – A$_t$) *versus* time, where A$_\infty$ and A$_t$ are the molar absorbances at 'infinity' and time t, respectively. The k$_1$ values are listed in Tables I and II as a function of pressure for the respective complex ions, Pt(dien)Br$^+$ and Pt(dien)Cl$^+$, at various solution compositions. These values represent the average calculated from two to five individual experiments, with an average error in each constant of ±1.3%.

TABLE I. Pressure Dependence of the Rate Constant k_1 for the Hydrolysis of $Pt(dien)Br^+$ at 25 °C.

Pressure, bar	10^4 k_1 s^{-1}					
	Concentration of Added Salt[a]					
	$0^{b,c}$	0.2 *M*[c] ($LiClO_4$)	0.2 *M*[c] ($NaClO_4$)	0.2 *M*[c] (NaBr)	0^d	0.2 *M*[d] ($NaClO_4$)
1	1.44	1.30	1.34	1.45	1.37	1.28
125			1.39			1.37
250	1.58	1.46	1.48	1.58	1.49	1.44
375						1.52
500	1.83	1.60	1.63	1.73	1.66	1.61
750	1.99	1.80	1.81	1.89	1.82	1.76
1000	2.18	1.96	1.98	2.08	2.01	1.93
1250	2.39	2.22	2.17	2.32	2.26	2.14
1500	2.66	2.35	2.37	2.49	2.47	2.27
1750			2.59			2.50

[a] [NaOH] = 10^{-2} *M*, unless otherwise indicated. [complex] = 2 × 10^{-3} *M*. [b] [NaOH] = 5 × 10^{-3} *M*. [c] Complex was used in the form [Pt(dien)Br] Br. [d] Complex was used in the form [Pt(dien)Br] ClO_4.

TABLE II. Pressure Dependence of the Rate Constant k_1 for the Hydrolysis of [Pt(dien)Cl] Cl at 25 °C.

Pressure, bar	10^4 k_1 s^{-1}		
	[$NaClO_4$][a] (*M*)		
	0	0.2 *M*	1.0 *M*
1	1.04	1.00	0.872
150		1.06	0.928
250	1.16	1.11	0.989
500	1.27	1.20	1.09
750	1.44	1.39	1.13
1000	1.64	1.53	1.34
1250	1.80	1.68	1.44
1400	1.85		
1500		1.79	1.58
1750	2.19		

[a] [complex] = 1.25 × 10^{-3} *M* and [NaOH] = 0.01 *M*.

All the plots of ln k_1 *versus* pressure were linear within the very narrow experimental error limits. These data were therefore submitted to a linear least-squares analysis and the resulting $\Delta V_1^{\neq}$ values are given in Table III.

Discussion

The appearance of strong curvature in the ln k_1 *versus* pressure plot in the original investigation [3] of the hydrolysis of $Pt(dien)Br^+$ can be traced to a fault in the spectrophotometric equipment used at that time. The single-beam instrument has the inherent disadvantage of being directly dependent on the stability of the light source intensity. This becomes a critical factor for relatively slow reactions (*e.g.* in this case the reaction has a half life of *ca.* 86 min at atmospheric pressure) and may result in large systematic errors in the rate constants. At much higher pressures, or in the presence of substituting nucleophiles, where the rate of reaction is considerably faster [3], this problem is no longer significant. In fact, with the new 'split-beam' version of the apparatus the reaction of $Pt(dien)Cl^+$ with N_3^- was reinvestigated [8] and an identical $\Delta V_2^{\neq}$ value for the second-order reaction path [3] was obtained.

To reinforce the argument that the curvature seen previously [3] was the result of systematic experimental errors – the average absolute error in each rate constant was 3.8%, despite the fact that seven runs were conducted at each pressure – a linear-least squares treatment of the original data yields a $\Delta V_1^{\neq}$ for –9.6 ± 0.6 cm^3 mol^{-1} for the complex, [Pt(dien)Br] Br, in 0.2 *M* $NaClO_4$ at 25 °C. This value is clearly in good agreement with the corresponding $\Delta V_1^{\neq}$ in Table III of –9.3 ± 0.1 cm^3 mol^{-1}.

A comparison of the $\Delta V_1^{\neq}$'s shown in Table III for the bromide and perchlorate salts of $Pt(dien)Br^+$ at the respective $NaClO_4$ concentrations of zero and 0.2 *M* demonstrates that the nature of the counter ion is not an important factor. The decrease in the absolute value of $\Delta V_1^{\neq}$ upon increasing the [$NaClO_4$] is shown more clearly in the corresponding data in Table III for the chloro complex although the effect is again very small, lying just outside the range of the experimental errors. Sodium perchlorate has a strong structure-breaking

TABLE III. Volumes of Activation at 25 °C.

Complex	[Added Salt] (M)	Nature of Salt	$\Delta V_1^{\neq}$ (cm^3 mol^{-1})
[Pt(dien)Br] Br	0	–	–10.0 ± 0.3
	0.2	$LiClO_4$	–9.8 ± 0.3
	0.2	$NaClO_4$	–9.3 ± 0.1
	0.2	NaBr	–9.0 ± 0.2
[Pt(dien)Br] ClO_4	0	–	–9.7 ± 0.1
	0.2	$NaClO_4$	–9.2 ± 0.2
[Pt(dien)Cl] Cl	0	–	–10.5 ± 0.3
	0.2	$NaClO_4$	–9.9 ± 0.3
	1.0	$NaClO_4$	–9.3 ± 0.4

effect on water [9] and, consequently, tends to decrease the difference in volume between the bulk solvent and coordinated water. As the addition of $NaClO_4$ only amounts to a small reduction in the absolute value of $\Delta V_1^{\neq}$, one can conclude that the intrinsic volume decrease associated with Pt–OH_2 bond formation dominates this term. It is of interest to note that the $\Delta V_2^{\neq}$'s for the direct associative attack of such nucleophiles as N_3^-, NO_2^- and pyridine, are similar to $\Delta V_1^{\neq}$, *viz.* –8.5 ± 0.2, –6.4 ± 0.7 and –7.7 ± 0.5 cm^3 mol^{-1} ($\mu = 0.2\,M$ ($NaClO_4$), 25 °C) [3], respectively. Apparently electrostriction plays only a minor role in these reactions. On the basis of these results alone, a common mechanism could be assumed for the k_1 and k_2 paths, namely an A mechanism.

This work also reveals that $\Delta V_1^{\neq}$, as well as $\Delta V_2^{\neq}$ [3], is pressure independent, as least up to 1.75 kbar, within the very narrow experimental error limits of the individual rate constants. Nevertheless, if the quadratic expression $\ln k_1 \doteq a + bP + cP^2$ is used to fit these data, $\Delta\beta_1^{\neq}$ values ranging from –2.2 to +0.8 cm^3 mol^{-1} $kbar^{-1}$ result, *i.e.* $\Delta\beta_1^{\neq} = 2cRT$.

According to Stranks' model [10], in this system an A mechanism should correspond to the migration of a water molecule from the more compressible bulk medium to the first coordination sphere of the complex during the activation process. Consequently, $\Delta V_1^{\neq}$ must become less negative with increasing pressure and $\Delta\beta_1^{\neq} < 0$, *e.g.* for a 3+ complex ion, $\Delta\beta^{\neq}$ was calculated to be –0.72 cm^3 mol^{-1} $kbar^{-1}$ per water molecule. Clearly the variations in $\Delta\beta_1^{\neq}$ observed here make it of little use as a mechanistic criterion in these reactions. Moreover, notwithstanding the relatively low pressures applied in this research, the fact that $\Delta\beta^{\neq}$ values of the order of 2 cm^3 mol^{-1} $kbar^{-1}$ can be obtained from pressure data for which extremely good *linear* fits of lnk *versus* pressure are found – giving rise to errors in $\Delta V_1^{\neq}$ of only ±0.1 cm^3 mol^{-1} in two cases – must cast some doubt on the value of $\Delta\beta^{\neq}$ as a sound mechanistic parameter.

If direct interaction occurs between the anions in solution and the Pt(II) center of the complex, this should influence $\Delta V_1^{\neq}$. Interaction of this type would be expected to be much stronger for Br^- ions than for ClO_4^- ions. However, as mentioned earlier, both the bromide and perchlorate salts of the complex exhibit identical $\Delta V_1^{\neq}$'s and even in the presence of 0.2 M NaBr the change in $\Delta V_1^{\neq}$ parallels the change caused by adding 0.2 M $NaClO_4$. This is fully consistent with the structure-breaking characteristics of NaBr which are similar to those of $NaClO_4$ [9]. In this context it is interesting to note that the presence of structure-promoting Li^+ ions tends to offset the destructive nature of the ClO_4^- ions so that the $\Delta V_1^{\neq}$ value for $LiClO_4$ closely resembles that in water. However, these differences are small and must therefore be kept in the right perspective. On the other hand, solvent molecules, particularly protic ones, are known to preferentially solvate such Pt(II) complexes [11]. This preassociation may well eliminate the need for a further solvent molecule to penetrate the coordination sphere of the complex, thereby resulting in $\Delta V_1^{\neq}$ values significantly less than the partial molar volume of water. In addition, no substantial change in the overall compressibility of the system need occur.

Finally, the simplified solvation model [10] used to rationalize $\Delta\beta^{\neq}$ values in terms of a particular reaction mechanism may be suspect, especially in view of more recent work [12] which shows that a layer of 'unstructured' water exists between the bulk solvent and the solvation sheath.

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