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Kinetics and Mechanism of some Fast Anation Reactions of a Series of Substituted dien Complexes of Palladium(II). pH Dependency in Neutral and Basic Aqueous Solutions

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The anation kinetics of a series of methyl and ethyl substituted dien aquo complexes of palladium(II) by iodide were studied at 5 < pH < 9, and in some cases at 9 < pH < 12, in order to investigate the substitution behaviour of the corresponding hydroxo complexes. The anation rate constant decreases significantly with increasing pH and fits for 5 < pH < 9 a mechanism in which the aquo complex is the only reactive species. The deviations from this mechanism at pH > 9 are ascribed to secondary reactions involving the hydroxo and/or some conjugate-base species.

Introduction

We recently reported the temperature and pressure dependencies of some fast anation reactions of a series of palladium(II)-substituted dien complexes in weakly acidic aqueous solution [1]. The pH of the solutions was adjusted to values sufficiently lower than the pK_a values of the aquo complex species to prevent possible participation of the corresponding hydroxo species. The present investigation focuses on the reactivity of the latter species, since no literature information could be found. The aquo and hydroxo complex ions are related to each other by a simple acid–base equilibrium $[Pd(L)(H_2O)]^{2+} \rightleftharpoons [Pd(L)(OH)]^+ + H^+$ (L = substituted dien) so that a pH dependence study should give a decisive answer as to whether the hydroxo species can also undergo direct substitution as with the corresponding aquo species. The pK_a values of the aquo complexes fall within the range 7.0 to 7.5 [1], so that a pH dependence study of the substitution process at $5 < pH < 9$ was undertaken to obtain the desired information. The process was in some cases studied at pH > 9 since complications were expected to occur under such conditions, due to possible deprotonation of the dien ligand to produce conjugate-base species of completely different kinetic behaviour. This was the reason for adopting a spectrophotometric method in determining the pK_a values of the aquo complexes as outlined previously [1]. Finally, the present study offered a means of extrapolating substitution data measured at high pH to obtain anation data at low pH for aquo complexes normally too labile to be studied under such conditions.

Experimental

The complexes, instrumentation and kinetic procedures were the same as before [1]. An additional requirement was the selection of a suitable buffer to control the pH of the test solutions. Preliminary experiments showed that for unbuffered solutions the $[OH^-]$ released during substitution is capable of increasing the pH, for instance, from 6.5 to 9.6. The pH was found to be effectively stabilized over the range $6 < pH < 10$ by Tris (= trishydroxymethylaminomethane) buffer solutions, whereas the pH of the reacting solutions remained virtually constant over the range $10 < pH < 12$, so that no buffer was required.

Results and Discussion

A number of preliminary kinetic measurements were performed to establish whether the selected buffer had any effect on the complex solution prior to mixing with the ligand solution in the stopped-flow apparatus. Although no significant UV/visible spectral changes were observed for the aquo/hydroxo species concerned, a fairly slow substitution reaction interfering with the substitution process under study (and causing major deviations from expected kinetic values) was observed. The complication could, how-

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TABLE I. pH Dependence of Anation Reaction of Substituted dien Complexes. [Pd] = 1 × 10^{-3} mol dm^{-3}, ionic strength = 0.1 mol dm^{-3}, temperature = 25 °C, wavelength = 400 nm.

Complex	$[I^-]$ mol dm^{-3}		k_{obs}/s^{-1}							
			pH = 5	pH = 6	pH = 7	pH = 8	pH = 9	pH = 10	pH = 11	pH = 12
$[Pd(1,4,7\text{-}Me_3dien)(H_2O)]^{2+}$	1 × 10^{-2}						148 ± 4	45.6 ± 0.3		
	3 × 10^{-2}							57.8 ± 0.7		
	5 × 10^{-2}							76.4 ± 0.3		
		k_o/s^{-1}						36.8 ± 3.2		
		$k/dm^3\ mol^{-1}\ s^{-1}$:					(1.48 ± 0.04) × 10^4	771 ± 94		
$[Pd(1,4,7\text{-}Et_3dien)(H_2O)]^{2+}$	1 × 10^{-2}						87.5 ± 1.1	17.6 ± 0.4	6.99 ± 0.06	
	3 × 10^{-2}						241 ± 8	29.6 ± 0.5	10.7 ± 0.1	5.27 ± 0.12
	5 × 10^{-2}							42.1 ± 0.7	14.1 ± 0.3	6.07 ± 0.05
		k_o/s^{-1}						11.4 ± 0.2	5.25 ± 0.12	4.07 ± 0.06
		$k/dm^3\ mol^{-1}\ s^{-1}$:					8393 ± 196	614 ± 7	178 ± 4	40.0 ± 0.6
$[Pd(1,1,4\text{-}Et_3dien)(H_2O)]^{2+}$	1 × 10^{-2}			154 ± 3	118 ± 3	25.4 ± 0.2	3.54 ± 0.02	0.618 ± 0.004		
	3 × 10^{-2}					78.2 ± 0.8	11.4 ± 0.3	1.10 ± 0.01		
	5 × 10^{-2}					129 ± 3	18.1 ± 0.3	1.43 ± 0.01		
		k_o/s^{-1}						0.440 ± 0.076		
		$k/dm^3\ mol^{-1}\ s^{-1}$:				2576 ± 33	366 ± 6	20.4 ± 2.2		
$[Pd(1,1,7,7\text{-}Me_4dien)(H_2O)]^{2+}$	1 × 10^{-2}		87.1 ± 4.5	63.5 ± 0.9	43.1 ± 0.4	15.4 ± 0.2	2.97 ± 0.03			
	2 × 10^{-2}		149 ± 3							
	3 × 10^{-2}			190 ± 3	150 ± 3	44.9 ± 0.8	8.13 ± 0.08			
	5 × 10^{-2}					76.8 ± 0.6	13.1 ± 0.1			
		$k/dm^3\ mol^{-1}\ s^{-1}$:	8081 ± 287	6346 ± 89	4644 ± 72	1524 ± 20	276 ± 2			
$[Pd(1,1,4,7,7\text{-}Me_5dien)(H_2O)]^{2+}$	1 × 10^{-2}		42.6 ± 1.9	33.1 ± 0.1	19.7 ± 0.1	5.54 ± 0.04	1.18 ± 0.03			
	2 × 10^{-2}		81.2 ± 3.2							
	3 × 10^{-2}			93.5 ± 0.6	60.2 ± 0.5	16.7 ± 0.1	2.78 ± 0.01			
	5 × 10^{-2}			153 ± 1	104 ± 1	27.1 ± 0.1	4.15 ± 0.01			
		$k/dm^3\ mol^{-1}\ s^{-1}$:	4162 ± 174	3164 ± 15	2018 ± 11	551 ± 3	98 ± 1			

ever, be overcome by adding the buffer to the ligand solution instead of to the complex solution prior to mixing.

The rate constants obtained for the substitution of a series of palladium(II) substituted dien complexes by iodide as a function of pH and $[I^-]$ are presented in Table I. On the one hand it was expected, on the basis of earlier anation studies [1–3], that the pseudo-first-order rate constants k_{obs} might vary linearly with $[I^-]$. On the other hand the substitution of hydroxide by iodide, in the case where the hydroxo species itself undergoes substitution, might follow the normal two-term rate-law [4]. In the latter case the solvolysis path k_o is linked to the intercept and the direct substitution route k to the slope of the k_{obs} *versus* $[I^-]$ plot. Results showed that, as described in more detail below, for $5 < pH < 9$ the former and for $9 < pH < 12$ the latter expectation was met.

The data in Table I for $pH < 9$ show a linear relationship between k_{obs} and $[I^-]$, *i.e.* $k_{obs} = k[I^-]$, possibly indicating that only anation is operative in the range $5 \leq pH < 9$ and that the significant decrease in the values of k with increasing pH is simply due to a decrease in the fraction of complex ion available as aquo species. In such case it should be possible to fit the data to a mechanism of the type

$$\begin{tikzcd}{[Pd(L)(H_2O)]^{2+}} \arrow[r, shift left, "K"] \arrow[d, "I^-"', "k_{anation}"] & {[Pd(L)(OH)]^+ + H^+} \arrow[l, shift left] \\ {[Pd(L)I]^+ + H_2O} & \end{tikzcd}$$

L = substituted dien

for which $k_{obs} = k_{anation}\,[I^-]\,f_{aquo}$

$$= k_{anation}\,[I^-]\,[H^+]/\{K + [H^+]\}$$

or

$$k = k_{anation}\,[H^+]/\{K + [H^+]\}$$

or

$$1/k = 1/k_{anation} + K/k_{anation}\,[H^+].$$

This implies that a plot of $1/k$ *versus* $1/[H^+]$ should be linear and that the values of K and $k_{anation}$ determined from the intercept and slope should be in agreement with those measured directly [1]. Figure 1 illustrates that such plots are indeed linear for the 1,1,4-Et_3, 1,1,7,7-Me_4 and 1,1,4,7,7-Me_5 species in the range $5 \leq pH \leq 8$, while Table II indicates that the values of K and $k_{anation}$ obtained from these plots are in fairly good agreement with those measured before. It is thus concluded that substitution by iodide in this pH range proceeds only *via* the anation reaction path and that no direct reaction occurs between iodide ion and the hydroxo complex. A direct consequence is that anation rate data, not measurable at low pH because the substitution reaction becomes too fast, can be obtained by extrapolation of substitution rate data measured at high pH. This is demonstrated by the prediction in Table II of $k_{anation}$ for 1,1,4-Et_3 species that is not directly measurable at $pH < 6$ (*cf.* Table I).

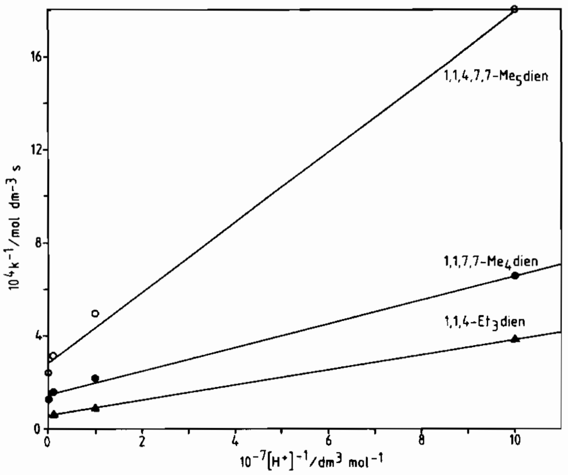

Fig. 1. Graphical verification of suggested anation model. [Pd] = 1×10^{-3} mol dm^{-3}, ionic strength = 0.1 mol dm^{-3}, temperature = 25 °C.

The data in Table I for $pH > 9$ deviate from what applies at $pH < 9$. Firstly, plots of k_{obs} *versus* $[I^-]$ have intercepts k_o which are relatively small at pH = 9 but become more significant at $10 < pH < 12$, as shown for instance by the entries for the 1,4,7-Et_3 species. There are two possible reasons for this observation; either the hydroxo species itself undergoes substitution *via* a solvolysis mechanism and/or a reverse hydrolysis reaction of the iodo product species contributes towards k_{obs}. The latter possibili-

TABLE II. Values of K and $k_{anation}$ from Suggested Anation Model.

Complex	$k_{anation}$/dm^3 mol^{-1} s^{-1}		pK	
	estimated[a]	experimental[b]	estimated[a]	experimental[b]
$[Pd(1,1,4\text{-}Et_3dien)(H_2O)]^{2+}$	17513 ± 1564	[c]	7.24 ± 0.05	7.12 ± 0.01
$[Pd(1,1,7,7\text{-}Me_4dien)(H_2O)]^{2+}$	6849 ± 563	8081 ± 287	7.45 ± 0.05	7.54 ± 0.01
$[Pd(1,1,4,7,7\text{-}Me_5dien)(H_2O)]^{2+}$	3425 ± 364	4162 ± 174	7.28 ± 0.06	7.29 ± 0.02

[a] From plot of $1/k$ *versus* $1/[H^+]$ (*cf.* Fig. 1). [b] Previously measured [1]. [c] Too fast to be measured [1].

ty is supported by spectral measurements indicating that the forward substitution reaction does not go to completion at high pH, even when the ratio $[I^-]/[OH^-]$ exceeds 100 in most cases. Secondly, the slopes k of the k_{obs} *versus* $[I^-]$ plots deviate from those extrapolated from the anation model based on the lower pH data (pH < 8). For instance, the values of k estimated for the 1,4,7-Et_3 species at pH = 10 and pH = 11 are 13 and 1 $dm^3\ mol^{-1}\ s^{-1}$ respectively, which are significantly lower than the experimental values of 614 and 178 $dm^3\ mol^{-1}\ s^{-1}$ respectively. This deviation indicates that either the hydroxo species undergoes a direct substitution reaction not observable at lower pH, and/or a conjugate-base species originating from deprotonation of the dien ligand exhibits enhanced reactivity at high pH.

Since the discussed deviations are not significant at pH = 9, the data reported in Table I for the 1,4,7-Me_3 and 1,4,7-Et_3 species at this pH can be used to calculate, with the aid of the anation model equation derived above and the pK values determined previously [1], the value of $k_{anation}$ for these species. They are 1.3×10^6 and 4.9×10^5 $dm^3\ mol^{-1}\ s^{-1}$ respectively and confirm the reactivity pattern 1,4,7-Me_3dien > 1,4,7-Et_3dien > 1,1,4-Et_3dien > 1,1,7,7-Me_4dien > 1,1,4,7,7-Me_5dien, in agreement with the increasing extent of steric hindrance.

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