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Substitution Kinetics of Palladium(II)diethylenetriamine Complexes in Basic Medium

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Abstract

Substitution reactions of the type $Pd(R_5dien)H_2O^{2+} + I^- \rightarrow Pd(R_5dien)I^+ + H_2O$ (R = H, Me and Et) were studied as a function of steric hindrance in the range $7 \leqslant pH \leqslant 12$ in order to solve problems related to the nature of such reactions in basic medium. All the kinetic data can be interpreted in terms of an anation model in which the aqua complex is the only reactive species in this pH range. No evidence for conjugate base formation or for the participation of hydroxy bridged species was found. Deviations in the kinetic data at pH > 9 can be accounted for in terms of an increase in the fraction of the aqua complex resulting from a reverse aquation contribution of the iodo complex under such conditions.

Introduction

Our interest in the substitution behaviour of diethylenetriamine (dien) and substituted dien complexes of palladium(II) has led to a series of studies dealing with the effect of steric hindrance on the intimate nature of solvolysis, anation and ligand substitution reactions [1–3]; the pH dependence of anation reactions [4]; the inability of coordinated hydroxide to undergo CO_2 uptake reactions [5]; the relevance of such processes in antitumor activity of related complexes [6, 7]; the labilization of the dien ligand in acidic medium or under influence of coordinated sulfite [8, 9]; spontaneous solvolysis reactions [10]; the influence of the leaving group on the solvolysis process [11]; and the solvent dependence of this process [12]. A fascinating aspect of the investigated reactions concerns the substitution and addition inertness of complexes of the type $Pd(R_5dien)OH^+$, where R = H, Me or Et, notwithstanding the low nucleophilicity of hydroxide. In this respect it is noteworthy that such species are usually not produced via a direct ligand substitution process (for instance Cl^- for OH^-) but rather via rate-determining solvolysis (aquation) followed by rapid deprotonation in basic medium (pH > 8) [3]. Evidence for base-catalyzed substitution reactions of square planar complexes involving conjugate base species, has also been reported by several groups in the past [3, 4, 13–18].

In order to throw more light on the substitution behaviour of such hydroxo complexes, we previously investigated the pH dependence of a few typical anation reactions [4]. The results demonstrated that the kinetic data in the range $5 \leqslant pH \leqslant 9$ could be fitted with a model in which only the $Pd(R_5dien)H_2O^{2+}$ species undergoes anation with no significant contribution from substitution via the conjugate base species $Pd(R_5dien)OH^+$. At higher pH (>9), however, significant deviations were observed, but the limited data did not allow a detailed interpretation. In the meantime, we have extended these measurements up to pH 12, and can now report our findings for the overall acidity range $7 \leqslant pH \leqslant 12$. These enable us to comment on the observed deviations in detail. Furthermore, recent work [19] has reemphasized the possible participation of hydroxy-bridged complexes in such systems, especially in the region of the pK_a value, and a reanalysis of our earlier and present data came into question. A detailed account of our findings for a series of substitution reactions of $Pd(R_5dien)H_2O^{2+}$ by iodide as a function of pH will be given in this contribution.

Experimental

The various $Pd(R_5dien)Cl^+$ complexes were synthesized according to standard procedures [20] and converted to the corresponding aqua complexes by the addition of $AgClO_4$ as described before [1, 4]. The aqua complexes were characterized in solution by comparing their UV/Vis spectral data with

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published values [1, 3, 21]. In addition, the purity of such solutions could also be confirmed by the pH titrations performed in order to determine the pK_a values of the aqua complexes. All experiments were carried out at 25 °C and an ionic strength of 0.1 mol dm^{-3} adjusted with $NaClO_4$. The incoming ligand (I^-) was used in at least a ten fold excess to ensure pseudo-first-order conditions. TRIS buffer* was employed to stabilize the pH in the range $7 \leqslant pH \leqslant 9$. Since it is known that TRIS buffer can react with such complexes, special precautions were taken to avoid possible interference of the buffer, e.g. the buffer was added only to the ligand containing solution prior to mixing. Previous studies showed that I^- reacts *ca.* 200 times faster than TRIS with the investigated complexes [21, 22], so that a possible interference of the buffer can be neglected under such conditions.

UV/Vis spectra were recorded on Shimadzu UV 250, Perkin-Elmer Lambda 5 and Pye Unicam SP 1800 spectrophotometers. Kinetic experiments were performed on a Durrum D110 stopped-flow instrument equipped with a 2 cm optical path length mixing cell, a receiver vessel into which a pH electrode was mounted to measure the pH of the reaction mixture immediately after the reaction, and a data acquisition system enabling the immediate conversion of the absorbance *versus* time trace into a first-order plot [23]. These plots were linear for at least two to three half-lives of the reaction, and the reported rate constants are mean values of at least four determinations.

Results and Discussion

Before we present the kinetic data measured in this study, it is important to consider the possible equilibria in solution. These can be summarized as follows

$$Pd(R_5dien)H_2O^{2+} \overset{K_a}{\rightleftharpoons} Pd(R_5dien)OH^{+} + H^{+} \qquad (1)$$

$$Pd(R_5dien)H_2O^{2+} + Pd(R_5dien)OH^{+} \overset{K}{\rightleftharpoons} (R_5dien)Pd(\mu\text{-}OH)Pd(R_5dien) + H_2O \qquad (2)$$

Equilibrium (1) represents the acid dissociation process and equilibrium (2) the suggested formation of a dimeric hydroxy bridged species. The latter species reaches a maximum concentration at $pH = pK_a$, *i.e.* where the aqua and hydroxo complexes are present in the ratio 1:1 [19]. Martin and coworkers used the irregular nature of the pH titration curve to estimate a K value of 132 $dm^3\ mol^{-1}$ for the unsubstituted dien complex [24]. Using this result, it can be shown that the maximum concentration of the dimeric species amounts to 0.018 mol dm^{-3} at $pH = pK_a = 7.74$ and a [total Pd(II)] = 0.06 mol dm^{-3}. However, this concentration reduces to 3×10^{-5} mol dm^{-3} for [total Pd(II)] = 1×10^{-3} mol dm^{-3} as used in this study, *i.e.* a mere 3% of the total Pd(II) content. This concentration reduces drastically at pH lower or higher than the pK_a value [19]. A similar K value was recently reported [19] for the corresponding platinum(II) complex. In the light of these results it is quite understandable that we could not observe any kinetic evidence for the participation of such a dimeric species in our previous study since the [total Pd(II)] was never higher than 1×10^{-3} mol dm^{-3}. The same applies for the present study.

The kinetic data for the anation reactions of a series of substituted dien complexes as a function of pH are summarized in Table 1. The results exhibit the expected trends: k_{obs} increases with increasing $[I^-]$; k_{obs} decreases with increasing steric hindrance; and k_{obs} decreases with increasing pH. Plots of k_{obs} *versus* $[I^-]$ are linear and go through the origin for $pH < 9$ ($pH \leqslant 9$ in some cases), but exhibit meaningful intercepts at $pH > 9$. The slope of such plots represents the overall second-order rate constant k for the anation process according to the mechanism outlined in eqn. (3). Under pseudo-first-order conditions, k_{obs} can be expressed as in eqn. (4), and rewritten as in eqn. (5).

$$\begin{tikzcd} Pd(L)H_2O^{2+} \arrow[r, phantom, "\overset{K_a}{\rightleftharpoons}"] \arrow[d, "k_{an}", "+I^-"'] & Pd(L)OH^{+} + H^{+} \\ Pd(L)I^{+} + H_2O & \end{tikzcd} \qquad (3)$$

$$k_{obs} = k_{an}[I^-][H^+]/\{K_a + [H^+]\} = k[I^-] \qquad (4)$$

where $k = k_{an}[H^+]/\{K_a + [H^+]\}$

$$k^{-1} = k_{an}^{-1} + K_a/k_{an}[H^+] \qquad (5)$$

It follows that the anation rate constant (k_{an}) can be calculated by plotting k^{-1} *versus* $[H^+]^{-1}$. Such plots are linear at $pH \leqslant 9$ and result in the k_{an} and K_a data summarized in Table 2. The values of k_{an} demonstrate the effect of steric hindrance on the anation process. The results are in good agreement with values of k_{an} that could in some cases be measured directly by performing the anation reaction at pH 5 [3, 4, 25]. Furthermore, K_a could be determined spectrophotometrically as described before [1], and the results are in good agreement with the values extracted from the pH dependence of k. These trends are in good agreement with our earlier findings for $pH \leqslant 9$.

At higher pH the data exhibit meaningful deviations. Firstly, plots of k_{obs} *versus* $[I^-]$ exhibit

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*TRIS = tris(hydroxymethyl)aminomethane.

TABLE 1. Rate Data for the Anation of $Pd(L)H_2O^{2+}$ by I^- as a Function of Steric Hindrance and pH[a]

L	$10^2 \times [I^-]$ (mol dm^{-3})		k_{obs} (s^{-1})					
			pH = 7.0 ± 0.1	pH = 8.0 ± 0.1	pH = 9.0 ± 0.1	pH = 10.0 ± 0.1	pH = 11.0 ± 0.1	pH = 12.0 ± 0.1
1,4,7-Me_3dien	1				148 ± 4	45.6 ± 0.3	24.6 ± 1.7	20.1 ± 0.7
	2						27.7 ± 2.1	20.5 ± 0.5
	3					57.8 ± 0.7	30.7 ± 1.4	21.0 ± 0.7
	4						34.2 ± 1.3	21.3 ± 0.3
	5					76.4 ± 0.3	37.7 ± 1.1	21.6 ± 0.8
		k_0 (s^{-1})				36.8 ± 3.2	21.2 ± 0.2	19.8 ± 0.1
		k (dm^3 mol^{-1} s^{-1})			(1.48 ± 0.04) × 10^4 [b]	771 ± 94[b]	327 ± 7	38.0 ± 2.3
1,4,7-Et_3dien	1				87.5 ± 1.1	17.6 ± 0.4	6.99 ± 0.06	5.42 ± 0.18
	2						8.69 ± 0.08	5.65 ± 0.10
	3				241 ± 8	29.6 ± 0.5	11.1 ± 0.4	5.91 ± 0.15
	4						12.4 ± 0.3	6.07 ± 0.05
	5					42.1 ± 0.7	14.0 ± 0.1	6.25 ± 0.09
		k_0 (s^{-1})				11.4 ± 0.2	5.32 ± 0.33	5.24 ± 0.04
		k (dm^3 mol^{-1} s^{-1})			(8.39 ± 0.20) × 10^3 [b]	614 ± 7[b]	177 ± 10	20.8 ± 1.1
1,1,4-Et_3dien	1		118 ± 3	25.4 ± 0.2	3.54 ± 0.02	0.618 ± 0.004	0.321 ± 0.002	0.214 ± 0.012
	2						0.377 ± 0.002	0.218 ± 0.016
	3			78.2 ± 0.8	11.4 ± 0.3	1.10 ± 0.01	0.434 ± 0.002	0.239 ± 0.015
	4						0.488 ± 0.008	0.251 ± 0.013
	5			129 ± 3	18.1 ± 0.3	1.43 ± 0.01	0.515 ± 0.003	0.256 ± 0.012
		k_0 (s^{-1})				0.440 ± 0.076	0.277 ± 0.011	0.201 ± 0.005
		k (dm^3 mol^{-1} s^{-1})	(1.18 ± 0.03) × 10^4 [b]	(2.58 ± 0.03) × 10^3 [b]	336 ± 6[b]	20.4 ± 2.2[b]	4.99 ± 0.34	1.17 ± 0.16
1,1,7,7-Me_4dien	1		43.1 ± 0.4	15.4 ± 0.2	2.97 ± 0.03	1.77 ± 0.01	0.680 ± 0.010	0.653 ± 0.011
	2		109 ± 9	37.8 ± 0.2	5.10 ± 0.09	1.83 ± 0.04	0.732 ± 0.058	0.661 ± 0.013
	3		160 ± 10	50.4 ± 0.4	8.40 ± 0.27	2.13 ± 0.08	0.775 ± 0.015	0.673 ± 0.013
	4		224 ± 3	73.3 ± 0.7	11.2 ± 0.07	2.17 ± 0.04	0.825 ± 0.013	0.689 ± 0.006
	5		290 ± 8	84.1 ± 1.2	13.2 ± 0.05	2.28 ± 0.11	0.862 ± 0.012	0.698 ± 0.010
		k_0 (s^{-1})				1.63 ± 0.07	0.638 ± 0.005	0.639 ± 0.003
		k (dm^3 mol^{-1} s^{-1})	(5.30 ± 0.50) × 10^3	(1.73 ± 0.12) × 10^3	275 ± 15	13.6 ± 2.2	4.57 ± 0.14	1.18 ± 0.07
1,1,4,7,7-Me_5dien	1		19.7 ± 0.1	5.12 ± 0.04	1.18 ± 0.03	0.997 ± 0.037	0.396 ± 0.017	0.344 ± 0.013
	2		40.6 ± 0.5	11.9 ± 0.1	1.78 ± 0.01	1.09 ± 0.04	0.431 ± 0.019	0.357 ± 0.013
	3		60.3 ± 0.1	15.5 ± 0.2	2.58 ± 0.21	1.15 ± 0.02	0.481 ± 0.037	0.363 ± 0.056
	4		78.0 ± 1.7	21.9 ± 0.1	2.95 ± 0.05	1.24 ± 0.03	0.517 ± 0.021	0.373 ± 0.028
	5		101 ± 3	25.1 ± 0.2	3.80 ± 0.36	1.33 ± 0.01	0.551 ± 0.010	0.385 ± 0.028
		k_0 (s^{-1})			0.535 ± 0.124	0.919 ± 0.037	0.356 ± 0.019	0.335 ± 0.002
		k (dm^3 mol^{-1} s^{-1})	(2.00 ± 0.30) × 10^3	534 ± 34	64.1 ± 3.7	8.10 ± 1.02	3.96 ± 0.52	0.980 ± 0.060

(continued)

TABLE 1. *(continued)*

L	$10^2 \times [I^-]$ (mol dm^{-3})		k_{obs} (s^{-1}) pH = 7.0 ± 0.1	pH = 8.0 ± 0.1	pH = 9.0 ± 0.1	pH = 10.0 ± 0.1	pH = 11.0 ± 0.1
1,1,7,7-Et$_4$dien	1						
	2		$(4.99 \pm 0.10) \times 10^{-2}$	$(1.61 \pm 0.03) \times 10^{-2}$	$(2.83 \pm 0.05) \times 10^{-3}$	$(6.76 \pm 0.06) \times 10^{-4}$	$(2.92 \pm 0.10) \times 10^{-4}$
	3		$(6.50 \pm 0.08) \times 10^{-2}$	$(2.44 \pm 0.02) \times 10^{-2}$	$(3.84 \pm 0.10) \times 10^{-3}$	$(7.48 \pm 0.04) \times 10^{-4}$	$(3.08 \pm 0.05) \times 10^{-4}$
	4		$(9.64 \pm 0.30) \times 10^{-2}$	$(3.17 \pm 0.04) \times 10^{-2}$	$(5.17 \pm 0.01) \times 10^{-3}$	$(7.97 \pm 0.04) \times 10^{-4}$	$(3.39 \pm 0.02) \times 10^{-4}$
	5		$(11.8 \pm 0.10) \times 10^{-2}$	$(3.79 \pm 0.01) \times 10^{-2}$	$(5.79 \pm 0.00) \times 10^{-3}$	$(8.68 \pm 0.06) \times 10^{-4}$	$(3.65 \pm 0.04) \times 10^{-4}$
		k_0 (s^{-1})			$(8.34 \pm 3.51) \times 10^{-4}$	$(5.54 \pm 0.23) \times 10^{-4}$	$(2.39 \pm 0.15) \times 10^{-4}$
		k (dm^3 mol^{-1} s^{-1})	2.36 ± 0.14	0.792 ± 0.024	0.102 ± 0.009	$(6.25 \pm 0.62) \times 10^{-3}$	$(2.50 \pm 0.42) \times 10^{-3}$
1,1,4,7,7-Et$_5$dien	1					$(5.29 \pm 0.01) \times 10^{-4}$	$(2.11 \pm 0.01) \times 10^{-4}$
	2		$(1.70 \pm 0.08) \times 10^{-2}$	$(5.58 \pm 0.01) \times 10^{-3}$	$(0.78 \pm 0.01) \times 10^{-3}$	$(6.07 \pm 0.09) \times 10^{-4}$	$(2.58 \pm 0.01) \times 10^{-4}$
	3		$(2.80 \pm 0.07) \times 10^{-2}$	$(7.77 \pm 0.01) \times 10^{-3}$	$(1.06 \pm 0.00) \times 10^{-3}$	$(6.90 \pm 0.28) \times 10^{-4}$	$(3.08 \pm 0.01) \times 10^{-4}$
	4		$(3.78 \pm 0.09) \times 10^{-2}$	$(10.9 \pm 0.03) \times 10^{-3}$	$(1.32 \pm 0.00) \times 10^{-3}$	$(7.64 \pm 0.10) \times 10^{-4}$	$(3.20 \pm 0.01) \times 10^{-4}$
	5		$(4.48 \pm 0.11) \times 10^{-2}$	$(13.6 \pm 0.02) \times 10^{-3}$	$(1.58 \pm 0.00) \times 10^{-3}$	$(8.49 \pm 0.13) \times 10^{-4}$	$(3.26 \pm 0.02) \times 10^{-4}$
		k_0 (s^{-1})			$(2.54 \pm 0.13) \times 10^{-4}$	$(4.49 \pm 0.06) \times 10^{-4}$	$(1.97 \pm 0.40) \times 10^{-4}$
		k (dm^3 mol^{-1} s^{-1})	0.906 ± 0.037	0.270 ± 0.008	$(2.66 \pm 0.00) \times 10^{-2}$	$(7.97 \pm 0.17) \times 10^{-3}$	$(2.91 \pm 1.19) \times 10^{-3}$

^{a}[Pd] = 0.001 mol dm^{-3}; T = 25 °C; ionic strength = 0.1 mol dm^{-3}; wavelength = 400 nm. ^{b}Data taken from ref. 1.

intercepts (k_0 in Table 1) which can either be due to a parallel or reverse reaction. In the latter case, aquation of the iodo complex will contribute to k_{obs} and account for the intercept at $[I^-] = 0$ mol dm^{-3}. The aquation reactions of the iodo products were studied separately by treating 1:1 mixtures of Pd(R_5dien)H_2O^{2+} and I^- with OH^-. The corresponding aquation rate constants are summarized in Table 3 along with the values of k_0 measured at high pH. It follows from the excellent agreement that the reverse aquation reaction of the iodo complex can account for the values of k_0.

The values of k at pH > 9 are higher than predicted by the mechanism in eqn. (3). This enhanced reactivity at higher pH can be seen from the plots in Fig. 1, where ln k is plotted *versus* $\ln\{[H^+]/(K_a + [H^+])\}$. According to eqn. (4), such a plot should be linear with unity slope and intercept ln k_{an}. The experimental values of k at pH > 9 deviate from the expected lines with unity slope, indicating that the mechanism in eqn. (3) cannot fully account for the high pH data. However, it must be kept in mind that the anation process is extremely slow under such conditions (low fraction of aqua complex) as seen from the values of k in Table 1. Nevertheless, the deviation is meaningful and must be accounted for.

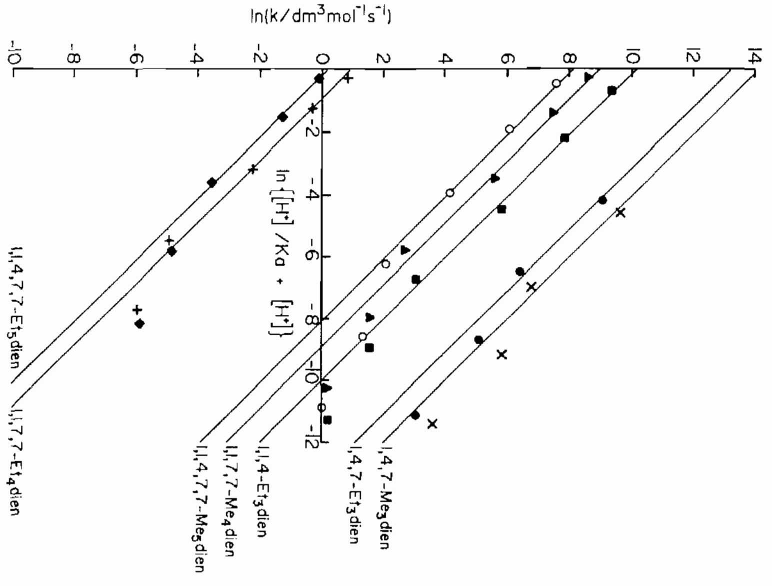

Fig. 1. Schematic illustration of the correlation between k and the fraction of the complex in the aqua form (data taken from Tables 1 and 2, lines of unity slope are drawn through the data at pH < 9).

TABLE 2. Experimental and Calculated pK_a Values for Complexes of the Type $Pd(L)H_2O^{2+}$ ($T = 25$ °C; ionic strength = 0.1 mol dm^{-3})

L	pK_a (exp.)[a]	pK_a (calc.)[b]	k_{an} (calc.)[b] (dm^3 mol^{-1} s^{-1})
1,4,7-Me_3dien	7.05		$(1.48 \pm 0.15) \times 10^6$
1,4,7-Et_3dien	7.24		$(5.44 \pm 0.53) \times 10^5$
1,1,4-Et_3dien	7.12	7.19	$(2.38 \pm 0.24) \times 10^4$
1,1,7,7-Me_4dien	7.54	7.53	$(7.25 \pm 0.67) \times 10^3$
1,1,4,7,7-Me_5dien	7.29	7.22	$(3.38 \pm 0.21) \times 10^3$
1,1,7,7-Et_4dien	7.60	7.52	2.96 ± 0.06
1,1,4,7,7-Et_5dien	7.47	7.44	1.21 ± 0.01

[a]Determined spectrophotometrically. [b]Calculated by means of eqn. (5) and data from Table 1.

TABLE 3. Comparison of Aquation Rate Constants of $Pd(L)I^+$ with Observed Intercepts of the Corresponding Anation Reaction at pH > 10[a]

L	$k_{aquation}$ (s^{-1})	k_0 (s^{-1})		$10^{-4} \times K$ ($=k_{an}/k_0$) (dm^3 mol^{-1})
		pH = 11.0 ± 0.1	pH = 12.0 ± 0.1	
1,4,7-Me_3dien	20.8 ± 0.1	21.2 ± 0.2	19.8 ± 0.1	7.12 ± 0.72
1,4,7-Et_3dien	5.48 ± 0.08	5.32 ± 0.33	5.24 ± 0.04	9.93 ± 1.05
1,1,4-Et_3dien	0.231 ± 0.001	0.277 ± 0.011	0.201 ± 0.005	10.3 ± 0.6
1,1,7,7-Me_4dien	0.653 ± 0.007	0.638 ± 0.005	0.639 ± 0.003	1.11 ± 0.11
1,1,4,7,7-Me_5dien	0.344 ± 0.007	0.356 ± 0.019	0.335 ± 0.002	0.983 ± 0.082
1,1,7,7-Et_4dien	$(2.37 \pm 0.05) \times 10^{-4}$	$(2.39 \pm 0.15) \times 10^{-4}$		1.25 ± 0.04
1,1,4,7,7-Et_5dien	$(1.95 \pm 0.05) \times 10^{-4}$	$(1.97 \pm 0.40) \times 10^{-4}$		0.621 ± 0.021

[a][Pd] = 0.001 mol dm^{-3}; $T = 25$ °C; ionic strength = 0.1 mol dm^{-3}; wavelength = 400 nm.

An obvious explanation for the enhanced lability at pH > 9 is the participation of a conjugate base species [4] originating from the deprotonation of the dien ligand. This could in principle account for the observed effect, if it was not for our observation that the fully substituted dien ligands (Me_5dien and Et_5dien) also exhibit the enhanced lability although they cannot produce conjugate base species. Their increase in reactivity is even larger than for the tetra-substituted dien ligands. Another possibility to account for the observed effect could involve hydrolysis reactions of iodide during which small fractions of a more reactive iodide species are produced. However, a series of experiments with chloride as anating ligand demonstrated similar deviations in the expected kinetic behaviour at pH > 9, indicating that it is unlikely that the formation of hydrolysis products can account for the observed effects.

A more plausible explanation may originate from the effect of the reverse aquation reaction of Pd(R_5dien)I^+ (*i.e.* k_0) on the fraction of aqua complex available in solution. This means that under conditions where a significant intercept (k_0) is observed, the product formation step is an equilibration through which the fraction of aqua complex may be increased, especially under conditions where this fraction is very low as indicated by the acid-dissociation constant K_a. The equilibrium constant K for the anation step can be calculated from k_{an}/k_0, and the values are summarized in Table 3. These values show a decrease with increasing steric hindrance, very similar to the opposite trend reported for the reverse solvolysis of a series of chloro complexes [10]. For an average value of 5×10^4 mol dm^{-3} it can be shown that the fraction of aqua complex present in this equilibrium equals $2 \times 10^{-5}/[I^-]$, and varies between 2×10^{-3} and 4×10^{-4} for the concentration range employed. Inspection of the data in Fig. 1 indicates that an increase in the fraction of aqua complex of *ca.* 5×10^{-4} will pull all the deviating data points at pH 11 and 12 back onto the expected lines. This means that a very small increase in the fraction of the aqua complex undergoing anation due to the reverse aquation step can account for the enhanced reactivity observed at pH > 9. In this respect it must be kept in mind that for a pK_a value of 7.5, the fraction of the aqua complex at pH 10, 11 and 12 is 3.1×10^{-3}, 3.2×10^{-4} and 3.2×10^{-5}, respectively. It follows that the increase of *ca.* 5×10^{-4} will especially affect the data at pH 11 and 12. Alternatively, it can be stated that due to the high value of K, the acid dissociation equilibrium is slightly shifted in the direction of the aqua species, and this is only observed under conditions where very little of the complex is in the aqua form.

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