Complex-formation Reactions of Aquacobalamin revisited: Effect of Chloride on the Rate and Activation Parameters

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Complex-formation reactions of aquacobalamin were reinvestigated to clarify the role of high chloride concentrations (up to 1 mol dm^{-3}). It was found that high chloride concentrations retard the reactions due to the formation of the less substitution-labile chloro complex, for which the formation constant was found to be 0.8 dm^3 mol^{-1} at 25 °C and ionic strength 1.0 mol dm^{-3}. The pH dependence of the complex formation with hydrazoic acid was also re-examined. Volumes of activation were determined for the reactions with HN_3 and N_3^- in $NaClO_4$ medium and are discussed in comparison with those measured in KCl medium. Direct kinetic evidence for the occurrence of a reverse, acid-catalysed aquation reaction was found and this step is characterised by an activation volume of +8.3 ± 1.6 cm^3 mol^{-1}. The results are all in agreement with the concept of a dissociative interchange substitution mechanism.

Complex-formation reactions of aquacobalamin (vitamin B_{12a}) and closely related systems have received significant attention from a number of kinetic groups in recent years.[1-11] It is now generally accepted that such reactions with a wide variety of nucleophiles all proceed according to a dissociative interchange, I_d, mechanism. Such a mechanism includes a rapid precursor formation equilibrium followed by a rate-determining interchange step. In some cases direct kinetic evidence for the participation of precursor species was reported.[5-11] Notwithstanding this apparently good agreement among the different kinetic groups, a number of discrepancies exists that we would like to point out and clarify in this contribution.

One aspect concerns the use of chloride salts to adjust the ionic strength of the test solutions. It is a general practice to perform complex-formation reactions of aquacobalamin at an ionic strength of 1.0–2.2 mol dm^{-3} adjusted with KCl.[1-8] We have recently shown that complex formation with 4-methylpyridine is *ca.* 3 times slower in 1.0 mol dm^{-3} KCl than in $NaClO_4$.[11] Such a large medium effect could be due to the partial formation of chloro complexes in the presence of KCl, at the expense of reactive aqua complexes, which would complicate the interpretation of the rate data and activation parameters. Another aspect concerns the pH dependence of complex-formation reactions with weakly acidic nucleophiles such as hydrazoic acid.[2] Such reactions can be affected by reverse, acid-catalysed aquation processes which can complicate the interpretation of the observed kinetic data. It was recently concluded on the basis of such data that activation parameters ($\Delta H^‡$, $\Delta S^‡$ and $\Delta V^‡$) cannot be employed for the system under consideration to distinguish between a dissociative interchange and a limiting dissociative mechanism.[2] However, this strongly opposes the well established and widely accepted mechanistic discrimination ability of especially $\Delta V^‡$.[9-13] We have, therefore, revisited some typical complex-formation reactions of cobalamin in an effort to clarify these apparent inconsistencies.

Experimental

Crystalline hydroxocobalamin hydrochloride (Fluka) was used to prepare the solutions of aquacobalamin. All solutions were prepared from Millipore water and stored in the dark at *ca.* 5 °C. The pH of the test solutions was adjusted with $HClO_4$ and NaOH, and measured before and after the reaction. Sodium perchlorate was generally used to adjust the ionic strength, unless otherwise indicated. The reference electrode of the pH-meter was filled with NaCl instead of KCl in order to prevent precipitation of $KClO_4$. All reagents were of analytical grade. In experiments where the chloride concentration was varied, NaCl was added to the aquacobalamin solution prior to the reaction with other nucleophiles.

The UV/VIS spectra were recorded on Cary 1 and HP 8452A spectrophotometers. All reactions were followed by characteristic absorbance changes on a Durrum D110 stopped-flow instrument. At high pressure (⩽150 MPa) a locally designed stopped-flow instrument, described elsewhere,[14] was used. Both instruments were run on-line with an IBM compatible personal computer. Data acquisition and handling were done with Biologic V3.23 (Claix, France) and OLIS KINFIT (Bogart, GA) software. All kinetic measurements were performed under pseudo-first-order conditions, *i.e.* an excess of nucleophile was employed. The reported pseudo-first-order rate constants are the averages from at least 10 kinetic runs.

Results and Discussion

Influence of High Chloride Concentrations.—In the present study we reinvestigated the complex-formation reactions of aquacobalamin, represented by $Co–H_2O^+$, with N_3^- and HN_3 in a $NaClO_4$ medium as compared to a KCl medium used before.[2] The pH profile for this reaction is characterised by the pK_a values of 4.1 and 7.9 for HN_3 and $Co–H_2O^+$, respectively.[2] A maximum rate constant is reached at pH 6.5, where $Co–H_2O^+$ and N_3^- are the main reactive species. Under these conditions a plot of k_{obs} *versus* total azide concentration for reaction (1) is

$$Co–H_2O^+ + N_3^- \xrightarrow{k_1} Co–N_3 + H_2O \qquad (1)$$

linear and without a significant intercept, indicating that the reaction goes to completion. The results obtained in the present study are reported in Fig. 1 as a function of pressure and the values of k_1 are summarised in Table 1. Our k_1 value of 678 ± 8 dm^3 mol^{-1} s^{-1} in $NaClO_4$ medium is significantly higher than that of 525 ± 14 dm^3 mol^{-1} s^{-1} reported for a KCl medium.[2] Furthermore, on introducing NaCl into the system the value of k_1 decreases steadily, in agreement with the mentioned trend.

Table 1 Rate and activation parameters for the reaction[a] $\text{Co–H}_2\text{O}^+ + \text{N}_3^- \xrightarrow{k_1} \text{Co–N}_3 + \text{H}_2\text{O}$

Ionic strength,[b] I/mol dm^{-3}	[Cl$^-$]/mol dm^{-3}	Pressure, p/MPa	k_1[c]/dm^3 mol^{-1} s^{-1}	$\Delta V^‡$/ cm^3 mol^{-1}
1.0	0	0.1	678 ± 8	+4.9 ± 0.3
		25	646 ± 5	
		50	620 ± 2	
		75	591 ± 6	
		100	568 ± 5	
		125	523 ± 5	
	0.3	0.1	640 ± 7	
	0.4		633 ± 6	
	0.5		624 ± 8	
0.10	0	25	1410 ± 80	+6.9 ± 0.3
		50	1310 ± 20	
		75	1210 ± 40	
		100	1130 ± 30	
		125	1070 ± 10	

[a] [Co–H$_2$O] = 5 × 10^{-5} mol dm^{-3}, [N$_3^-$] = 5 × 10^{-3}–3 × 10^{-2} mol dm^{-3}, 25.0 °C, pH 6.5. [b] Adjusted with NaClO$_4$. [c] Estimated from plots of k_{obs} *versus* [N$_3^-$].

Table 2 Rate and activation parameters for the reaction[a] $\text{Co–H}_2\text{O}^+ + \text{HN}_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Co–HN}_3^+ + \text{H}_2\text{O}$

pH	P/MPa	k_2[b]/ dm^3 mol^{-1} s^{-1}	k_{-2}[b]/s^{-1}	$\Delta V^‡$ (k_2)/ cm^3 mol^{-1}	$\Delta V^‡$ (k_{-2})/ cm^3 mol^{-1}
2.0	0.1	311 ± 2	1.6 ± 0.3	+9.4 ± 0.8	+8.3 ± 1.6
	25	306 ± 8	1.7 ± 0.2		
	50	288 ± 4	1.4 ± 0.1		
	75	265 ± 2	1.3 ± 0.1		
	100	238 ± 5	1.3 ± 0.3		
	125	209 ± 10	1.2 ± 0.3		
2.1	0.1	307 ± 4	1.5 ± 0.4		
2.5	0.1	300 ± 3	1.2 ± 0.1	+8.6 ± 0.4	
	25	315 ± 6	0.3 ± 0.2		
	50	292 ± 6	0.4 ± 0.2		
	75	270 ± 3	0.4 ± 0.1		
	100	247 ± 4	0.3 ± 0.1		
	125	222 ± 5	0.3 ± 0.1		
3.0	0.1	323 ± 10	0.6 ± 0.4	+8.3 ± 0.4	
	25	332 ± 3	—		
	50	312 ± 3	—		
	75	286 ± 5	—		
	100	263 ± 3	—		
	125	238 ± 2	—		

[a] [Co–H$_2$O] = 5 × 10^{-5} mol dm^{-3}, [HN$_3$] = 2 × 10^{-3}–5 × 10^{-2} mol dm^{-3}, 25.0 °C, I = 1.0 mol dm^{-3} (NaClO$_4$). [b] Estimated from $k_{\text{obs}} = k_{-2} + k_2\,[\text{HN}_3]$, see Disscussion.

According to the reported pH profile,[2] the reaction reaches a limiting rate constant at pH 2.0–3.0, which represents the condition where HN$_3$ is the main reactive species. Under these conditions plots of k_{obs} *versus* total azide concentration are linear but exhibit intercepts which depend on the selected pH (see Fig. 2). These intercepts are ascribed to an acid-catalysed aquation reaction and the kinetic data for the overall reaction (2) are summarized in Table 2. The intercepts (k_{-2}) can be

$$\text{Co–H}_2\text{O}^+ + \text{HN}_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Co–HN}_3^+ + \text{H}_2\text{O} \qquad (2)$$

measured rather accurately at pH 2.0, but become more difficult to measure at higher pH especially at elevated pressure. The values of k_2 are independent of pH in the range 2–3, and are markedly higher than the value of 103 ± 13 dm^3 mol^{-1} s^{-1} reported for the reaction in KCl medium.[2]

It follows from the above data that complex-formation reactions of aquacobalamin are significantly affected by the presence of chloride ions in solution. The effect for the reaction with N$_3^-$ is not as large as for the reaction with HN$_3$, where the rate constant is reduced by a factor of 3. A similar result was reported recently for the reaction with 4-methylpyridine, where the rate constant is three times smaller in 1.0 mol dm^{-3} KCl as compared to 1.0 mol dm^{-3} NaClO$_4$.[5,11] This suggests that the presence of Cl$^-$ has a larger influence in the case of the weaker nucleophiles HN$_3$ and 4-methylpyridine. We can account for these observations with the general reaction scheme outlined in (3) (Nu = nucleophile). The corresponding rate equation (4)

$$\begin{tikzcd}[column sep=large]
\text{Co–H}_2\text{O}^+ + \text{Cl}^- \arrow[rr, shift left, "K_3"] \arrow[dr, "{+\text{Nu},\ -\text{H}_2\text{O}}"', "k_4"] & & \text{Co–Cl} + \text{H}_2\text{O} \arrow[ll, shift left] \arrow[dl, "{+\text{Nu},\ -\text{Cl}}", "k_5"'] \\
& \text{Co–Nu}^+ &
\end{tikzcd} \qquad (3)$$

$$k_{\text{obs}} = \left(\frac{k_4 + k_5K_3[\text{Cl}^-]}{1 + K_3[\text{Cl}^-]}\right)[\text{Nu}] \qquad (4)$$

accounts for the decrease in the complex-formation rate constant with increasing [Cl$^-$] since it is reasonable to expect k_4 to be significantly larger than k_5 in terms of an I$_\text{d}$ mechanism. The [Cl$^-$] dependence data were fitted by equation (4) using k_4 = 678 ± 8 dm^3 mol^{-1} s^{-1} as measured in the absence of Cl$^-$

Table 3 Comparison of rate constants and activation volumes at 25 °C for the reaction $Co–H_2O^+ + Nu \underset{k_b}{\overset{k_a}{\rightleftharpoons}} Co–Nu^+ + H_2O$

Nu[a]	k_a/dm^3 mol^{-1} s^{-1}	$\Delta V^‡ (k_a)$/ cm^3 mol^{-1}	k_b/s^{-1}	$\Delta V^‡ (k_b)$/ cm^3 mol^{-1}	I^b/ mol dm^{-3}	Ref.
HN_3	103 ± 13	5.5 ± 0.3			1.0 (KCl)[c]	2
	311 ± 2	9.4 ± 0.8	1.6 ± 0.3	8.3 ± 1.6	1.0 ($NaClO_4$)[d]	*e*
	300 ± 3	8.6 ± 0.4	1.2 ± 0.1	—	1.0 ($NaClO_4$)[c]	*e*
	323 ± 10	8.3 ± 0.4	0.6 ± 0.4	—	1.0 ($NaClO_4$)[f]	*e*
py	34 ± 1	8.7 ± 1.4	2.3 ± 0.1	16.9 ± 0.8	0.5 ($NaClO_4$)	9
mpy	67 ± 2	8.2 ± 0.5	—	—	1.5 ($NaClO_4$)	11
apy	31 ± 2	9.7 ± 1.1	2.6 ± 0.1	12.2 ± 0.5	1.0 ($NaClO_4$)	11
tu	184 ± 5	9.1 ± 0.9	15.5 ± 0.4	6.7 ± 0.3	0.1 ($NaClO_4$)	10
dmtu	115 ± 2	6.7 ± 1.0	37.9 ± 0.2	10.0 ± 0.8	0.1 ($NaClO_4$)	10
N_3^-	525 ± 14	6.4 ± 0.1			1.0 (KCl)	2
	678 ± 8	4.9 ± 0.3			1.0 ($NaClO_4$)	*e*
	1410 ± 80	6.9 ± 0.3			0.1 ($NaClO_4$)	*e*
	927 ± 40	6.9 ± 0.2			0.5 ($NaClO_4$)	15

[a] Abbreviations: py = pyridine, mpy = 4-methylpyridine, apy = 3-acetylpyridine, tu = thiourea, dmtu = *N*,*N*′-dimethylthiourea. [b] Ionic medium is indicated in parentheses. [c] pH 2.5. [d] pH 2.0. [e] This work. [f] pH 3.0.

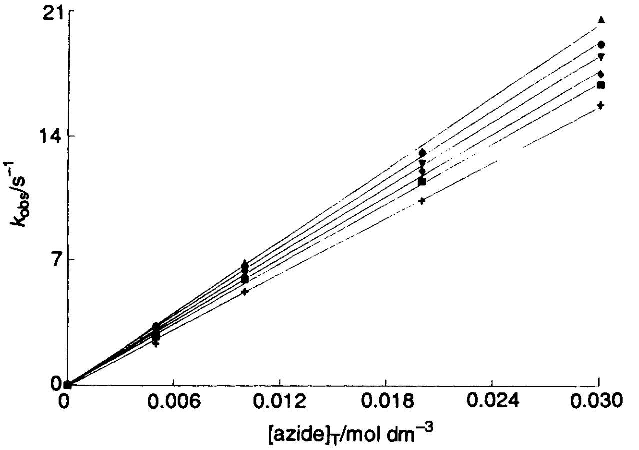

Fig. 1 Dependence of k_{obs} on the total azide concentration as a function of pressure for the substitution of aquacobalamin by azide. Experimental conditions: [Co] = 5 × 10^{-5} mol dm^{-3}, 25 °C, ionic strength = 1.0 mol dm^{-3} ($NaClO_4$), pH 6.5; p = 0.1 (▲), 25 (●), 50 (▼), 75 (◆), 100 (■) and 125 MPa (+)

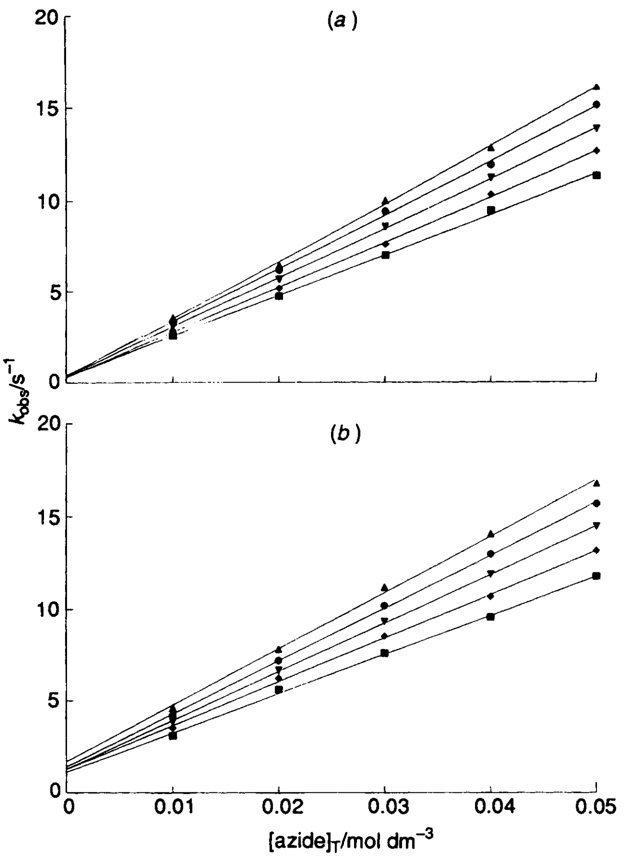

Fig. 2 Dependence of k_{obs} on the total azide concentration as a function of pressure for the substitution of aquacobalamin by hydrazoic acid. Experimental conditions: [Co] = 5 × 10^{-5} mol dm^{-3}, 25 °C, ionic strength = 1.0 mol dm^{-3} ($NaClO_4$), pH 2.5 (*a*) or 2.0 (*b*), p = 25 (▲), 50 (●), 75 (▼), 100 (◆) and 125 MPa (■)

and solving k_5 and K_3 from the k_{obs} values measured as a function of [Cl^-] and [N_3^-]. Six different fitting routines were employed, which all resulted in k_5 = 494 ± 10 dm^3 mol^{-1} s^{-1} and K_3 = 0.84 ± 0.05 dm^3 mol^{-1}. The value of K_3 is relatively small when compared with formation constants reported for complexes with stronger nucleophiles,[5,11] but large enough to cause an effective competition of chloride with other weak nucleophiles. A summary of some relevant complex-formation data is given in Table 3. The data clearly demonstrate the significant decrease in k_a for the reactions with HN_3 and N_3^- when the reaction medium is changed from 1.0 mol dm^{-3} $NaClO_4$ to 1.0 mol dm^{-3} KCl. From a comparison of the observed effects it can be concluded that $k_5 \approx 0$ for complex formation with HN_3. This means that a weak nucleophile such as HN_3 cannot substitute the co-ordinated Cl^-, whereas a stronger nucleophile like N_3^- can.

The volume of activation reported for complex formation with N_3^- in $NaClO_4$ medium, *viz.* +4.9 ± 0.3 cm^3 mol^{-1}, is smaller than that reported for a KCl medium, *viz.* +6.4 ± 0.1 cm^3 mol^{-1}.[2] This small effect is probably not surprising since the reaction of Co–Cl with N_3^- is only 20% slower than that of $Co–H_2O^+$ with N_3^- at 25 °C. However, there is a larger difference in the volumes of activation found for the reaction with HN_3 in $NaClO_4$ and KCl media, *viz.* in the absence of Cl^- $\Delta V^‡$ has an average value of +8.8 ± 0.5 cm^3 mol^{-1} in the range pH 2.0–3.0 compared to a value of +5.5 ± 0.3 cm^3 mol^{-1} in KCl medium (see Table 3). It is also important to note that, on changing the medium from $NaClO_4$ to KCl, $\Delta V^‡$ increases for complex formation with N_3^-, but decreases for complex formation with HN_3. The interpretation of the $\Delta V^‡$ data measured in KCl media is complex due to complications outlined above. Since $k_5 \approx 0$ for the reaction with HN_3 (see above), equation (4) simplifies to $k_{obs} = \{k_4/(1 + K_3[Cl^-])\}$[Nu]. Thus the effect of pressure on the complex-formation rate constant will be influenced by the effect of pressure on K_3 in the presence of Cl^-. It is reasonable to expect that $\Delta \bar{V}(K_3)$ will be small and positive due to the very similar partial molar volumes

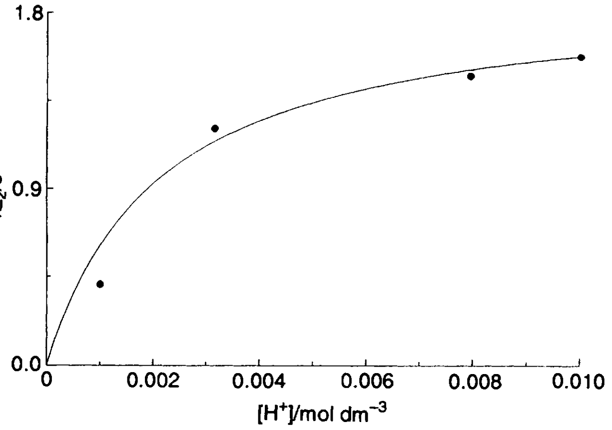

Fig. 3 A plot of k_{-2} *versus* $[H^+]$ for the reaction Co–HN_3 + H_2O^+ $\longrightarrow$ Co–H_2O^+ + HN_3. Experimental conditions: [Co] = 5×10^{-5} mol dm^{-3}, 25 °C, ionic strength = 1.0 mol dm^{-3} ($NaClO_4$)

of Cl^- (17.8 cm^3 mol^{-1})[16] and H_2O (18.0 cm^3 mol^{-1}) and since the overall reaction involves charge neutralisation.[12] Thus an increase in pressure will cause a decrease in K_3 (*i.e.* the equilibrium is shifted towards the aqua species) accompanied by an increase in k_{obs}, which results in a less-positive (more-negative) $\Delta V^\ddagger$ value in the presence of Cl^-.

The summary of rate and activation parameters in Table 3 indicates that on average the $\Delta V^\ddagger$ values are a few cm^3 mol^{-1} more positive for complex formation with neutral species than for the reaction with N_3^-. This may partly be related to some precursor formation in the latter case that could be accompanied by a small volume collapse. Notwithstanding this small difference, the values of $\Delta V^\ddagger(k_a)$ are all between +5 and +10 cm^3 mol^{-1}, which is very characteristic for an I_d mechamism controlled by the release of a water molecule.[12] The values of $\Delta V^\ddagger(k_a)$ do not show a specific ionic strength dependence, but do depend on the nature of the ionic medium as discussed above.

Interference from Acid-catalysed Aquation.—The complex-formation reactions with HN_3 were studied at low pH under which condition the plots of k_{obs} *versus* total azide concentration exhibit significant intercepts [see Figs. 2(*a*) and 2(*b*)]. These intercepts at ambient pressure clearly demonstrate a systematic increase in k_{-2} with increasing $[H^+]$ (see Table 2), which reaches a limiting value at $[H^+]$ = 0.01 mol dm^{-3} (see Fig. 3). These results demonstrate that the reverse reaction, acid-catalysed aquation, follows the sequence in equations (5) and (6), for which the rate equation is (7). A non-linear least-squares

$$\text{Co–N}_3 + \text{H}^+ \overset{K_6}{\rightleftharpoons} \text{Co–HN}_3^+ \quad (5)$$

$$\text{Co–HN}_3^+ + \text{H}_2\text{O} \xrightarrow{k_7} \text{Co–H}_2\text{O}^+ + \text{HN}_3 \quad (6)$$

$$k_{-2} = k_7K_6[\text{H}^+]/(1 + K_6[\text{H}^+]) \quad (7)$$

fit of the data resulted in $K_6 = 467 \pm 70$ dm^3 mol^{-1} and $k_7 = 1.9 \pm 0.1$ s^{-1} at 25 °C. Despite this evidence for an acid-catalysed reaction, there is no evidence for a spontaneous aquation reaction, since at higher pH no intercept is observed (see Fig. 1). The value of K_6 corresponds to a pK_a value for Co–HN_3^+ of 2.7, which is very reasonable in view of the pK_a value of unco-ordinated HN_3 (4.1). To our knowledge, this is the first evidence reported for an acid-catalysed aquation reaction of complexes of cobalamin.

The pressure dependence of k_{-2} at pH 2.0 corresponds to that of k_7 and the $\Delta V^\ddagger$ value of $+8.3 \pm 1.6$ cm^3 mol^{-1} is very close to the value of $+9.4 \pm 0.8$ cm^3 mol^{-1} found for the reverse complex-formation reaction (see Table 2). This means that the extent of bond breakage during the release of HN_3 or H_2O must be rather similar on the basis of an I_d mechanism. The partial molar volume of HN_3 was estimated to be 36.8 cm^3 mol^{-1} from the partial molar volume of NaN_3 (28.0 cm^3 mol^{-1})*[,16] and the reaction volume for $HN_3 \rightleftharpoons H^+ + N_3^-$ (−7.6 cm^3 mol^{-1}).[17] It is significantly larger than that of water, but since HN_3 will be co-ordinated in a linear way the volume increase during Co–HN_3 bond breakage could be very similar to that for Co–H_2O bond breakage. This is also seen in the overall reaction volume for reaction (2), *viz.* $\Delta V^\ddagger(k_2) - \Delta V^\ddagger(k_{-2}) = (9.4 \pm 0.8) - (8.3 \pm 1.6) = 1.1 \pm 1.8$ cm^3 mol^{-1}, which is practically zero notwithstanding the large difference in partial molar volume between HN_3 and H_2O. Thus the decrease in volume during the co-ordination of HN_3 is cancelled by the increase in volume during the release of H_2O and *vice versa*.

We conclude that the results of this study have helped to resolve a number of apparent inconsistencies. We have clearly demonstrated that a chloride medium significantly affects the fraction of the reactive aqua complex available to participate in the complex-formation reaction. Furthermore, a more detailed analysis of such reactions at lower pH has indicated that acid-catalysed reverse aquation reactions can interfere with the interpretation of rate and activation parameters for complex-formation reactions. All the reported activation volumes clearly underline the validity of a dissociative interchange mechanism, in line with conclusions reached in other investigations.[1–8,10,11]

Acknowledgements

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie, as well as a stipend from Deutscher Akademischer Austauschdienst to F. F. P. that enabled him to participate in this work.

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* Measured on an Anton Paar densimeter at 25.0 °C over the concentration range (1.3–3.6) $\times 10^{-3}$ mol dm^{-3}.

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Received 22*nd August* 1994; *Paper* 4/05115G