Mechanism of Complex Formation: A Kinetic Study of the Gallium(III)–Salicylate Ion System

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The kinetics of the reaction between gallium(III) and salicylic acid have been investigated by the temperature-jump technique at 25 °C. The measurements have been made in acid solution (pH 1.3—3) in order to avoid precipitation and to minimise polymerisation The results are interpreted according to a reaction scheme consisting of five parallel paths: the species Ga^{3+}, $[Ga(OH)]^{2+}$, and $[Ga(OH)_2]^+$ react with the salicylate ion, and $[Ga(OH)]^{2+}$ and $[Ga(OH)_2]^+$ react with salicylic acid, all giving rise to a 1 : 1 complex $[Ga(OC_6H_4CO_2)]^+$. The path involving $[Ga(OH)_2]^+$ and salicylate ion proceeds through an intermediate $[Ga(OH)(OC_6H_4CO_2)]$. Among the reaction paths proposed, two pairs exhibit proton ambiguity; therefore, only upper limits for their rate constants can be estimated. The rate constants for the hydrolysed species are considerably larger than those for Ga^{3+}. The equilibrium constant for the complex formation has been determined, both spectrophotometrically and kinetically, in the range pH 1.8—3.2.

WITH the exception of reactions of Fe^{III},[1-5] few rapidly reacting systems involving tervalent metal ions have been studied. This may be due to the fact that hydrolysis and polymerisation complicate the interpretation of the kinetic results. In particular, the only complex-formation reactions investigated involving cations of Group 3B concern the systems Al^{III}, Ga^{III}, and In^{III} with sulphate,[6,7] Al^{III} with salicylate,[8] sulphosalicylate,[9] $[Fe(CN)_6]^{3-}$,[10] and $[Co(CN)_6]^{3-}$,[11] Ga^{III}, In^{III}, and Tl^{III} with semixylenol orange,[12] and In^{III} with murexide.[13]

The present study of the reaction between gallium(III) and salicylate ions has been undertaken in order to study the kinetic behaviour of an ion for which the mechanism of water exchange seems to deviate from the usual scheme,[14] and whose mechanism of complex formation may therefore be expected to differ from that advanced by Eigen[15] for the formation of labile complexes.

EXPERIMENTAL

Gallium(III) perchlorate was prepared either by anodic dissolution of the metal in an aqueous solution containing perchloric acid or by dissolving 99.9% Ga_2O_3 in 1 mol dm^{-3} $HClO_4$. The solid was precipitated by evaporating the solution and twice recrystallised from water. Other chemicals were of analytical grade. Salicylic acid was recrystallised from water. Conductivity water was used to prepare the solutions and as a reaction medium. Stock solutions of $Ga[ClO_4]_3$ contained a small amount of $HClO_4$ in order to prevent hydrolysis and polymerisation, and were titrated with ethylenediaminetetra-acetic acid (H_4edta).[16] The equilibrium quotients of the gallium(III)–salicylate complex were determined by use of a Hilger–Gilford spectrophotometer, whereas the kinetic experiments were carried out in a temperature-jump apparatus constructed by Messanlagenstudiengesellschaft m.b.H., Göttingen. The magnitude of the jump was *ca.* 3.3 °C. The reaction was followed spectrophotometrically at 310 nm. The relaxation times were evaluated manually with a device developed in this department.[17] For each reaction mixture, up to four jumps were performed and the spread of the τ values was $<10\%$.

The desired values of pH were obtained by adding small amounts of $HClO_4$ or Na[OH] and measured by a Metrohm E 500 digital pH meter. The hydrogen-ion concentrations were derived from the measured pH with the aid of the Davies equation[18] using $B = 0.2$. All the measurements were carried out at 25 °C and an ionic strength of 0.1 mol dm^{-3} ($Na[ClO_4]$).

RESULTS

Equilibrium Constant.—When gallium(III) ion is added to a solution of salicyclic acid, H_2A, a change in the spectrum of the acid is observed. The band at 300 nm is shifted to higher wavelengths and the absorbance increases. The extent of this change is small and depends on the pH; nevertheless it is of sufficient magnitude to allow spectrophotometric determinations to be carried out (Figure 1).

The equilibrium between the reactants and the complex is dependent on acidity; however, under our experimental conditions the hydrogen-ion concentration is sufficiently high for its change during complex formation to be negligibly small and the system can be represented by reaction (1).

$$Ga_f + A_f \underset{k_d}{\overset{k_f}{\rightleftharpoons}} GaA \qquad (1)$$

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The apparent pH-dependent equilibrium quotient of this reaction is as in (2). In the following, $[A^{2-}]$ in equation (4)

$$K_{\text{app.}} = [\text{GaA}]/[\text{Ga}_f][\text{A}_f] \tag{2}$$

where

$$[\text{Ga}_f] \equiv [\text{Ga}^{3+}] + [\text{Ga(OH)}^{2+}] + [\text{Ga(OH)}_2{}^{+}] \tag{3}$$

$$[\text{A}_f] \equiv [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}] \tag{4}$$

is neglected since the second dissociation constant of salicylic acid is very small ($\text{p}K_{\text{A}2}$ 13).[19]

Das *et al.*[20] showed that the molar ratio between Ga^{III} and salicylic acid in the complex is 1 : 1. We have confirmed this finding by the Job method at different acidities. The value of $K_{\text{app.}}$ was measured in two ways.

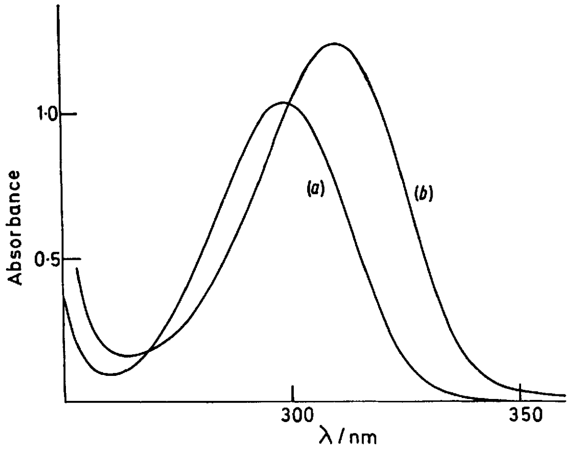

FIGURE 1 Absorption spectra of aqueous solutions at pH 2.8 containing (*a*) 10^{-4} mol dm^{-3} salicylic acid and (*b*) 10^{-4} mol dm^{-3} salicylic acid and 3×10^{-2} mol dm^{-3} gallium(III) perchlorate

(*a*) Spectrophotometric measurements were made at 310 nm and different concentrations of the reactants, with $c(\text{Ga}^{\text{III}}) = c_{\text{A}} = c$, at eight values of pH between 2.0 and 3.2. The degree of association, α, is given by expression (5)

$$\alpha = \frac{(A/c - \varepsilon_{\text{A}})}{\varepsilon_{\text{GaA}} - \varepsilon_{\text{A}}} \tag{5}$$

where A is the absorbance and ε_{A} and ε_{GaA} were measured in the absence and in the presence of a strong excess of gallium, respectively. Introduction of α into equation (2) gives the required $K_{\text{app.}}$. At pH < 2 the extent of complex formation is too small for reliable values of α to be obtained. The results are reported in Table 1. Each value of $K_{\text{app.}}$ quoted in the Table was obtained as a mean from up to six measurements made at a range of concentrations of the reactants between 1.5×10^{-4} and 4×10^{-4} mol dm^{-3}.

(*b*) The dependence of the reciprocal relaxation time on reactant concentration is given by expression (6) with [21] k_f/k_d

$$1/\tau = k_f([\text{Ga}_f] + [\text{A}_f]) + k_d \tag{6}$$

$= K_{\text{app.}}$. The value of $K_{\text{app.}}$ was evaluated from this equation by an iterative procedure: as a first approximation, the stoicheiometric concentrations of the reactants were substituted for $[\text{Ga}_f]$ and $[\text{A}_f]$ and approximate values of k_f and k_d were obtained. From these, new better trial values for $[\text{Ga}_f]$ and $[\text{A}_f]$ were obtained and introduced in equation (6), and so on. Convergence to within 0.1% was usually reached after three or four iterations. The results (Table 2) at six values of pH between 1.8 and 3.0 were treated in this way; again, at pH < 1.8, the complex is too weak, and k_f was too small, for reliable results to be obtained (see Figure 2 which shows the dependence of $1/\tau$ on the equilibrium concentration, for four values of pH).

TABLE 1

Apparent formation quotients, $K_{\text{app.}}$, of the gallium(III)–salicylate complex at different acidities, 25 °C, $I = 0.1$ mol dm^{-3} (Na[ClO$_4$]), and 310 nm

pH	ε_{GaA} / 10^3 mol^{-1} cm^2	ε_{A} / 10^3 mol^{-1} cm^2	$K_{\text{app.}}$ / dm^3 mol^{-1}
2.0	3 970	2 904	0.196
2.2	3 970	2 900	0.380
2.5	3 970	2 800	1.12
2.7	3 970	2 640	1.87
2.8	3 970	2 600	2.37
2.9	3 970	2 560	2.92
3.0	3 970	2 550	2.87
3.2	3 970	2 450	6.41

TABLE 2

Forward (k_f) and reverse (k_d) rate constants for the reaction between gallium(III) and salicylate ions at different acidities, 25 °C, and $I = 0.1$ mol dm^{-3}

$10^2[\text{H}^+]$ / mol dm^{-3}	$10^{-3}k_f$ / dm^3 mol^{-1} s^{-1}	k_d / s^{-1}
6.45	0.251	4.62
5.13	0.191	4.45
3.24	0.249	3.25
2.04	0.243	3.65
1.29	0.472	3.57
0.813	1.31	3.49
0.407	5.27	2.72
0.204	8.15	4.60
0.129	16.1	6.50

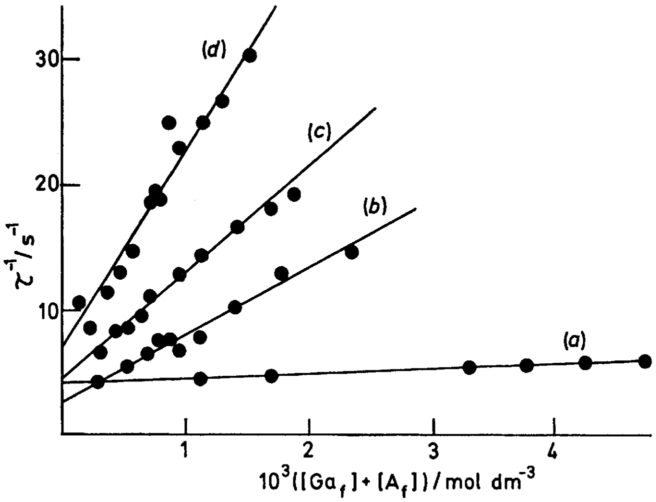

FIGURE 2 Plots of $1/\tau$ as a function of the sum of the concentrations of uncomplexed gallium and salicylate ions at 25 °C and $I = 0.1$ mol dm^{-3} (Na[ClO$_4$]) at pH 1.3 (*a*), 2.5 (*b*), 2.8 (*c*), or 3.0 (*d*)

The agreement between the two methods was fair (if we

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disregard one value of k_d which is obviously too low). The pH dependence of $K_{app.}$ is given by (7). With[8] $K_A = 2.04 \times 10^{-3}$ mol dm^{-3}, and K_{H1} and K_{H2} equal to 1.23×10^{-3} and 2.10×10^{-4} mol dm^{-3}, respectively,[22] from equation (7) we obtained $K_1 = 15.6$ as a mean from eight spectrophotometric and five kinetic results, with a standard deviation of the individual points of ± 3.0.

$$K_{app.} = K_1K_A[H^+]/\{(K_A + [H^+])([H^+]^2 + K_{H1}[H^+] + K_{H1}K_{H2})\} \qquad (7)$$

where

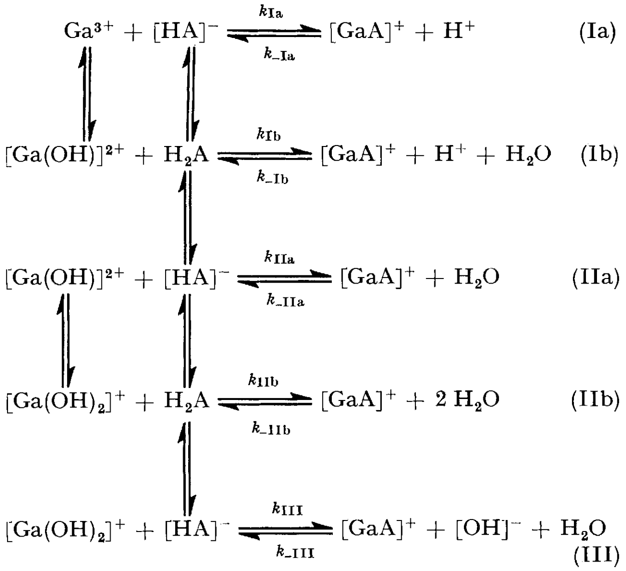
$$K_1 = [GaA^+][H^+]/[Ga^{3+}][HA^-] \qquad (8)$$

$$K_A = [H^+][HA^-]/[H_2A] \qquad (9)$$

$$K_{H1} = [Ga(OH)^{2+}][H^+]/[Ga^{3+}] \qquad (10)$$

$$K_{H2} = [Ga(OH)_2{}^+][H^+]/[Ga(OH)^{2+}] \qquad (11)$$

Kinetic Results.—Table 2 give the values of k_f and k_d for nine values of pH, derived as explained under (*b*) in the previous section (see also Figure 2). The Table shows that whereas k_f increases continuously with decreasing acidity, k_d passes through a minimum. This suggests that three parallel reaction paths of order 1, 0, and -1 in [H$^+$], respectively are operative in the reverse reaction and that three forms of Ga^{III} with increasing reactivity, *i.e.* Ga^{3+}, [Ga(OH)]$^{2+}$, and [Ga(OH)$_2$]$^+$, are involved in the forward reaction. A reaction scheme which is compatible with these conclusions is given by reactions (I)—(III). Since the vertical protolytic equilibria are fast in comparison with complex formation, this scheme leads to equations (12) and (13). Combining these expressions with equation (2), we obtain (14).*



$$\mathrm{Ga^{3+} + [HA]^- \underset{k_{-Ia}}{\overset{k_{Ia}}{\rightleftharpoons}} [GaA]^+ + H^+} \qquad (Ia)$$

$$\mathrm{[Ga(OH)]^{2+} + H_2A \underset{k_{-Ib}}{\overset{k_{Ib}}{\rightleftharpoons}} [GaA]^+ + H^+ + H_2O} \qquad (Ib)$$

$$\mathrm{[Ga(OH)]^{2+} + [HA]^- \underset{k_{-IIa}}{\overset{k_{IIa}}{\rightleftharpoons}} [GaA]^+ + H_2O} \qquad (IIa)$$

$$\mathrm{[Ga(OH)_2]^+ + H_2A \underset{k_{-IIb}}{\overset{k_{IIb}}{\rightleftharpoons}} [GaA]^+ + 2\,H_2O} \qquad (IIb)$$

$$\mathrm{[Ga(OH)_2]^+ + [HA]^- \underset{k_{-III}}{\overset{k_{III}}{\rightleftharpoons}} [GaA]^+ + [OH]^- + H_2O} \qquad (III)$$

On the basis of equation (14), a statistical analysis[23] was applied to 90 runs, at nine values of pH between 1.3 and 3.0, and reactant concentrations between 10^{-4} and 10^{-3} mol dm^{-3}.

$$k_f = (k_1'[H^+] + k_2' + k_3'[H^+]^{-1})K_{app.}/K_1 \qquad (12)$$

$$k_d = (k_1'[H^+] + k_2' + k_3'[H^+])^{-1}/K_1 = k_{-1}'[H^+] + k_{-2}' + k_{-3}'[H^+]^{-1} \qquad (13)$$

$$\frac{(1/\tau)K_1}{K_{app.}([Ga_f] + [A_f]) + 1} = k_1'[H^+] + k_2' + k_3'[H^+]^{-1} \qquad (14)$$

For each pH, $K_{app.}$ was calculated from equation (7). The results are $k_1' = k_{Ia} + (k_{Ib}K_{H1}/K_A) = (6.7 \pm 0.6) \times 10^2$ dm^3 mol^{-1} s^{-1}, $k_2' = k_{IIa}K_{H1} + (k_{IIb}K_{H1}K_{H2}/K_A) = 42 \pm 2$ s^{-1}, and $k_3' = k_{III}K_{H1}K_{H2} = (5.2 \pm 0.3) \times 10^{-2}$ mol dm^{-3} s^{-1}. It follows that $k_{-1}' = k_{-Ia} + k_{-Ib} = k_1'/K_1 = 43$ dm^3 mol^{-1} s^{-1}, $k_{-2}' = k_{-IIa} + k_{-IIb} = k_2'/K_1 = 2.8$ s^{-1}, and $k_{-3}' = k_{-III}K_W = k_3'/K_1 = 3.40 \times 10^{-3}$ mol dm^{-3} s^{-1}.

We have also obtained the rate parameters of the reverse reactions without making use of the synthesised values of $K_{app.}$. By a least-squares treatment of equation (13), using the data reported in Table 1, we obtain $k_{-1}' = 38 \pm 10$ dm^3 mol^{-1} s^{-1}, $k_{-2}' = 2.2 \pm 0.4$ s^{-1}, and $k_{-3}' = (5.0 \pm 0.9) \times 10^{-3}$ mol dm^{-3} s^{-1}, in reasonable agreement with the above results. This confirms the validity of our assumptions.

DISCUSSION

Reaction paths involving A^{2-} can be ruled out because of the extremely low relative concentration of this substance. Similarly, the reaction involving Ga^{3+} and H$_2$A has not been included in our reaction scheme because the observed pH dependence provides no evidence for such a reaction.

Reactions (Ia) and (Ib) are kinetically indistinguishable and $k_1' = k_{Ia} + (k_{Ib}K_{H1}/K_A)$. We can calculate an upper limit for k_{Ia} if we assume k_{Ib} to be negligibly small, and *vice versa*. Similarly, reactions (IIa) and (IIb) exhibit proton ambiguity and $k_2' = k_{IIa}K_{H1} + (k_{III}K_{H1}K_{H2}/K_A)$. Again, upper limits for k_{IIa} and k_{IIb} can be calculated. The results are shown in Table 3, together with results from previous investigations[6,12] which have been treated in a similar fashion.[12] All the values seem reasonable and it is very possible that both paths (a) and (b) contribute, and to similar extents.

According to the Eigen mechanism[15] an outer-sphere complex in equilibrium with the reactants is rapidly formed which is in turn converted into an inner-sphere complex in the subsequent, rate-determining, step. The key process of the latter step is the exit of a solvent molecule followed by penetration of the ligand in the vacated site and, in the present case, by fast ring closure. If this mechanism is operative, the rate of complex formation should be characteristic for the cation and independent of the nature of the ligand, apart from charge effects. Furthermore, the rate constant divided by K_{os}, the constant of outer-sphere complex formation, should be equal to the rate of water loss from the inner co-ordination shell (apart from a statistical factor which is not far from

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* This simple expression is obtained assuming that $\delta(Ga^{3+})/\{\delta(Ga^{3+}) + \delta[Ga(OH)^{2+}] + \delta[Ga(OH)_2{}^+]\}$ equals $[Ga^{3+}]/[Ga_f]$, and $\delta(HA^-)/[\delta(HA^-) + \delta(H_2A)]$ equals $[HA^-]/[A_f]$ (where δi is the difference between actual and equilibriun concentration of substance *i*). This is not strictly true in our unbuffered solutions, but the two correction terms arising from this fact are small and have opposite signs. The errors introduced by using equation (14) are largest at the highest values of pH, but are always <0.9%.

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unity[24]). We calculated rate constants for water loss, k_{H_2O}, and the outer-sphere complex formation constants, K_{os}, for our and other systems. The results are in Table 3 in which are also given the second-order rate constants for complex-formation reactions. The charge-dependent values of K_{os} were calculated from the Fuoss[25] equation correcting for the ionic strength with the aid of the Davies equation.[18] In the last column of Table 3 we show the values of k/K_{os} under the heading k_{H_2O}. They are all low in comparison with the value of k_{H_2O} of 18×10^2 s^{-1} obtained with the aid of ^{17}O n.m.r.[14] Furthermore, they are not ligand-independent as they should be if the Eigen mechanism is operative. This fact, together with the findings of Fiat and Connick,[14] makes it likely that the substitution reaction proceeds *via* an S_N2 mechanism. Fiat and Connick[14] concluded from the large negative value of $\Delta S^\ddagger$ for water exchange that this reaction does not proceed *via* the usual S_N1 mechanism, but *via* an expanded inner hydration shell.

TABLE 3

Values of k, K_{os}, and k_{H_2O} for reactions of Ga^{III} with various ligands, at 25 °C, and $I = 0.1$ mol dm^{-3} ($[HA]^-$ = salicylate ion, $[H_2B]^{2-}$ = semixylenol ion)

Metal ion	Ligand	$10^{-3}k$ / dm^3 mol^{-1} s^{-1}	K_{os} / dm^3 mol^{-1}	$10^{-2}k_{H_2O}$ / s^{-1}
Ga^{3+}	$[HA]^-$	$\leqslant 0.67$	5.3 [a]	$\leqslant 1.3$
	$[H_2B]^{2-}$	$\leqslant 0.69$ [b]	87 [a]	$\leqslant 0.08$
	$[SO_4]^{2-}$	20 [c]	*ca.* 1 000 [c]	*ca.* 0.2
		1.1 [d]	87 [a]	0.13
	H_2O	0.03		18 [e]
$[Ga(OH)]^{2+}$	H_2A	$\leqslant 1.1$	0.3 [a]	$\leqslant 30$
	$[HA]^-$	$\leqslant 34$	2 [a]	$\leqslant 170$
	$[H_3B]^-$	$\leqslant 1.1$ [b]	2	$\leqslant 5.5$
	$[H_2B]^{2-}$	12 [b]	13 [a]	9.2
	$[SO_4]^{2-}$	(100 [c])		
		14 [d]	13 [a]	11
$[Ga(OH)_2]^+$	H_2A	$\leqslant 350$	0.3	$\leqslant 1.1 \times 10^4$
	$[HA]^-$	210	1 [a]	2.1×10^3

[a] Calculated from the Fuoss equation[25] with $a = 5$ Å, and corrected for $I = 0.1$ mol dm^{-3} with the aid of the Davies equation.[18] [b] From ref. 12. [c] From ref. 6, at $I = 0.0$ mol dm^{-3}. [d] From ref. 6, corrected to $I = 0.1$ mol dm^{-3} with the aid of the Davies equation.[18] [e] From ref. 14.

In that case, the meaning of the values in the last column of Table 3 would not be k_{H_2O}; rather they would be the second-order rate constants which have been corrected for the charge effect, and divided by[25] $4\pi a^3N/3000 = 0.3$. The same correction brings the value for water to 1×10^2 s^{-1}. The values change in a manner which shows no obvious correlation with the basicity or nucleophilicity of the ligand, a fact which argues *against* an S_N2 mechanism. In conclusion, it seems that the question of the mechanism of substitution on Ga^{3+} cannot be definitely settled on the basis of the few data available in the literature.

It is interesting to note that, in contrast to reactions[26,27] involving the more substitution-labile cations Mg^{2+} and Ni^{2+}, and in common[9] with the much less labile Al^{3+} ion, the internal hydrogen bond in salicylic acid and its monoanion does not seem to exert any decelerating effect.

The rate constants for complex formation with $[Ga(OH)]^{2+}$ are all higher than those for Ga^{3+}, and those for $[Ga(OH)_2]^+$ may be higher still. This lends support to the Eigen mechanism, at least for the hydrolysed species. In that case, the labilising effect of $[OH]^-$ on the water molecules in the inner shell becomes important, an effect observed for many reactions involving tervalent cations.[1-11]

The rate constants of the reverse reactions all have reasonable values, with the exception of k_{-III} which, with $K_W = 1.58 \times 10^{-14}$ dm^6 mol^{-2}, we calculate to be 2.1×10^{11} dm^3 mol^{-1} s^{-1}. We must conclude that reaction (III) proceeds *via* an intermediate, [Ga(OH)A], in which one of the water molecules remaining in the inner shell has undergone hydrolysis. Path (III) in the reaction scheme can be replaced by (IV). The meaning of k_{-3}' then becomes not k_{-III}/K_W but rather the product of a first-order rate constant, for the decomposition of [Ga(OH)A] into metal and ligand, times an equilibrium constant $K_4 = [Ga(OH)A][H^+]/[GaA^+]$. Hydrolysis of the intermediate complexes has been observed, for instance,[28] for the malonate complexes of Cr^{III} and Co^{III}, and for $[FeCl]^{2+}$.[29] If the intermediate is taken into account, the numerator for the expression for $K_{app.}$, equation (7), should be multiplied by $(1 + K_4[H^+]^{-1})$. In our case, the fact that the presence of [Ga(OH)A] has not made itself felt in our equilibrium and rate measurements up to pH 3 means that K_4 must be considerably lower than 10^{-3} mol dm^{-3}, the hydrolysis constant of Ga^{3+}. This makes the rate constant for the decomposition of [Ga(OH)A] into reactants higher than that of $[GaA]^+$, but not unreasonably high.

$$[Ga(OH)_2]^+ + [HA]^- \underset{k_{-III}}{\overset{k_{III}}{\rightleftharpoons}} [Ga(OH)A] \underset{K_4}{\overset{H^+}{\rightleftharpoons}} [GaA]^+ + H_2O \quad \text{(IV)}$$

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