Mechanism of Complex Formation: Kinetics and Equilibria of the Gallium(III)–5-Nitrosalicylate Ion System

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The equilibria between gallium(III) and the 5-nitrosalicylate ion, HA^-, have been investigated by spectrophotometry in acid solution (pH 1—2.5). Two complexes are identified, their formation constants being $K_1 = [GaA^+][H^+]/[Ga^{3+}][HA^-] = 49 \pm 2$ and $K_1' = [Ga(HA)^{2+}]/[Ga^{3+}][HA^-] = 500 \pm 55$ dm^3 mol^{-1} at 25 °C and I =0.1 mol dm^{-3}. The kinetics of the formation and decomposition of the complexes have been investigated by the temperature-jump technique. The complex $[GaA]^+$ is formed in two pairs of 'proton-ambiguous' paths. Attributing the observed rate exclusively to the two reactions involving HA^- on the one hand, and Ga^{3+} and $[Ga(OH)]^{2+}$ on the other, one obtains upper limits for the rate constants, namely $(4.1 \pm 0.2) \times 10^2$ and $(6.4 \pm 0.7) \times 10^3$ dm^3 mol^{-1} s^{-1}, respectively. A fifth reaction, involving $[Ga(OH)]^{2+}$ and HA^-, makes a small contribution to the observed rate. The deprotonation of $[Ga(HA)]^{2+}$ is rapid in comparison with its formation from Ga^{3+} and HA^-. Comparison of the results with previous data provides evidence for an associative mechanism.

THE formation of labile octahedral complexes of bivalent metal cations is today universally recognised to proceed by the S_N1-ion pair or 'dissociative-interchange' mechanism,[1-4] originally assumed to be of general validity. On the other hand, for tervalent metal cations, evidence for an S_N2 or 'associative' mechanism is accumulating.[3-5] The gallium(III) ion is among the cations whose mechanism of complex formation is still somewhat in doubt. Comparatively little effort has so far been devoted to this cation.[6-10] Its study is complicated by the strong tendency of Ga^{3+} to undergo hydrolysis,[11,12] and also by the possibility of dimerisation [13] and polymerisation.[14]

We have recently [9] investigated the system gallium(III)-salicylate ion. Since ligand dependence (or independence) of the rate constant is one of the chief criteria which aid in the discrimination between associative and dissociative mechanisms,[1] the study of a ligand which has the same active site as the salicylate ion, but differs from it in its basicity,[5] should throw further light on the mechanism of complex formation by Ga^{III}. We chose the 5-nitrosalicylate ion for this purpose and abbreviated it as HA^-.

EXPERIMENTAL

A stock solution of gallium(III) perchlorate in excess of acid was prepared by anodic dissolution of the pure metal in dilute perchloric acid. A plate of smooth platinum with an area of *ca.* 4 cm^2 served as cathode. The current was 0.05 A and the distance between the electrodes was *ca.* 2 cm. Since under these conditions the Joule effect was sufficient to liquify the metal, the latter was kept in a small container immersed in the electrolysis cell, and electric contact was ensured by a platinum wire plunged into the fused metal. The amount of dissolved gallium was determined by weight. The concentration of the solution was then checked by ethylenediaminetetra-acetate (edta) titration, using pan [1-(2-pyridylazo)naphth-2-ol] as an indicator,[15] and was found to agree exactly with the electrogravimetric determination. Other chemicals were of analytical grade. Stock solutions of 5-nitrosalicylic acid (Fluka, purum) were prepared weekly. Triply distilled water was used throughout.

The hydrogen-ion concentration of the solutions was measured, when necessary, with a Radiometer PHM52 pH meter, having an accuracy of ±0.005 pH unit. The instrument was equipped with a combined glass electrode calibrated against perchloric acid of known concentration. All other measurements were carried out as described before.[9]

In the experiments designed to obtain the equilibrium constants, the concentration of Ga^{III}, c_M, was always at least 20 times that of the ligand, c_A, which was 2×10^{-5}—8×10^{-5} mol dm^{-3}.

In the kinetic measurements the concentrations of the ligand were varied between 5×10^{-5} and 2.5×10^{-4} mol dm^{-3} and those of the metal ion between 1×10^{-3} and 2×10^{-2} mol dm^{-3}, the higher concentrations being employed in the experiments at the higher hydrogen-ion concentrations.

The temperature was 25 °C throughout, and the ionic strength was 0.1 mol dm^{-3}.

RESULTS

Equilibrium Constants.—When gallium(III) ion is added to a solution of 5-nitrosalicylic acid, H_2A, a change in the spectrum of the acid is observed. The band at 310 nm is shifted to higher wavelengths and the absorbance increases. The extent of this change is larger than that observed in the gallium(III)–salicylate ion system.[9]

Under our conditions of excess of metal ion only 1 : 1 ligand to metal complexes are formed. We can define an apparent formation constant as the total complex concentration divided by the product of the concentrations of the total free Ga^{III}, Ga_f, and the total free ligand, A_f {equations (1) and (2), where $\alpha = (1 + [H^+]/K_{A1})$ and K_{A1} is the dissociation constant of H_2A}. The species A^{2-} has been neglected, since HA^- has a pK of 10.3,[16] and $[Ga_f]$ can be expressed as in equation (3), where $\beta = \{1 + (K_{H1}/[H^+]) + K_{H1}K_{H2}/[H^+]^2\}$, and K_{H1} and K_{H2} are the hydrolysis constants of Ga^{3+} and $[Ga(OH)]^{2+}$, respectively. In our

$$
\begin{aligned}
K_{\text{app.}} &= [\text{complex}]_T/[Ga_f][A_f] \\
&= [\text{complex}]_T/[Ga^{3+}][HA^-]\alpha\beta \qquad (1)
\end{aligned}
$$

$$[A_f] = [H_2A] + [HA^-] = [HA^-]\alpha \qquad (2)$$

$$
\begin{aligned}
&[Ga_f] = \\
&\quad [Ga^{3+}] + [Ga(OH)^{2+}] + [Ga(OH)_2{}^+] = [Ga^{3+}]\beta \qquad (3)
\end{aligned}
$$

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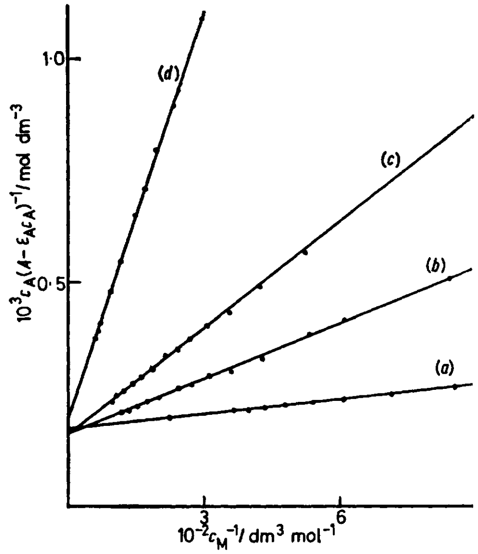


FIGURE 1 Plots of $c_A/(A - \varepsilon_A c_A)$ against the reciprocal of the gallium perchlorate concentration. $[H^+] = 0.01$ (*a*), 0.025 (*b*), 0.04 (*c*), and 0.09 mol dm^{-3} (*d*)

range of hydrogen-ion and gallium(III) concentrations the relative concentration of $[Ga(OH)_2]^+$ is always very small; [12] other species, such as dimers [13] and polymers,[14] can be neglected entirely. The method of Benesi and Hildebrand [17] was used to measure $K_{app.}$ Increasing amounts of $Ga[ClO_4]_3$ solution were added with a microsyringe to a solution of 5-nitrosalicylic acid of known concentration. Equation (1), together with Beer's law, yields relationship (4) where

$$\frac{c_A}{A - \varepsilon_A c_A} = \frac{1}{(\varepsilon_C - \varepsilon_A)} + \frac{1}{(\varepsilon_C - \varepsilon_A)K_{app.}} \times \frac{1}{c_M} \qquad (4)$$

A is the measured absorbance and ε_A and ε_C are the molar absorption coefficients of free and complexed ligand, respectively. A wavelength of 360 nm was found most suitable.

At constant hydrogen-ion concentration, a plot of the left-hand side of equation (4) as a function of $1/c_M$ should be a straight line. This was indeed found to be the case at 13 values of $[H^+]$, ranging between 3×10^{-3} and 9×10^{-2} mol dm^{-3}. Some examples are shown in Figure 1. The ratio of the intercept to slope yields $K_{app.}$ The intercepts change with $[H^+]$ because ε_A and ε_C are composite quantities which are pH dependent. From absorbance measurements in the absence of metal ion, ε_A was evaluated at various hydrogen-ion concentrations and, with the aid of the intercepts, values of ε_C were derived. The results are reported in Table 1.

TABLE 1

Apparent complex-formation constants, $K_{app.}$, and molar absorption coefficients, ε_A and ε_C at 360 nm, for the gallium(III)-5-nitrosalicylate ion system at different acidities

Run	$10^2[H^+]$/mol dm^{-3}	$10^{-2}K_{app.}$/dm^3 mol^{-1}	ε_A	ε_C	ε_C(calc.)
			dm^3 mol^{-1} cm^{-1}		
1	0.3	76 ± 3	3 850	9 980	9 610
2	0.4	66 ± 3	3 850	9 470	9 560
3 *	0.5	47 ± 3	3 750	9 800	9 500
4	0.75	26 ± 1	3 400	9 210	9 370
5 *	1.0	16 ± 0.5	3 000	8 820	9 250
6	1.5	8.9 ± 0.3	2 600	8 660	9 010
7	2.5	4.1 ± 0.3	2 500	8 630	8 800
8	3.0	3.2 ± 0.1	2 280	8 490	8 410
9	4.0	2.2 ± 0.1	2 240	8 300	8 090
10 *	5.5	1.3 ± 0.1	2 050	8 020	7 690
11	7.0	0.97 ± 0.1	1 900	6 550	7 362
12 *	7.5	0.80 ± 0.13	1 780	7 440	7 265
13	8.0	0.63 ± 0.08	1 800	7 560	7 174
14	9.0	0.65 ± 0.04	1 730	6 810	7 007

Runs marked with an asterisk have been repeated twice, and mean values are reported.

From Ga^{3+} and HA^- two complexes, $[Ga(HA)]^{2+}$ and $[GaA]^+$, can be formed with equilibrium constants defined as in equations (5) and (6). Using equations (1)—(3) and (5) and (6), we can write (7).

$$K_1 = [GaA^+][H^+]/[Ga^{3+}][HA^-] \qquad (5)$$

$$K_1' = [Ga(HA)^{2+}]/[Ga^{3+}][HA^-] \qquad (6)$$

$$K_{app.}\alpha\beta[H^+] = [\text{complex}]_T[H^+]/[Ga^{3+}][HA^-] = K_1 + K_1'[H^+] \qquad (7)$$

Figure 2 shows a plot of the left-hand side of equation (7) as a function of $[H^+]$ (filled circles), where α and β were calculated using the values $K_{A1} = 5.7 \times 10^{-3}$ mol dm^{-3} (ref. 5) and $K_{H1} = 1.23 \times 10^{-3}$ mol dm^{-3}.[12] A straight line with non-zero intercept is obtained which shows that both $[GaA]^+$ and $[Ga(HA)]^{2+}$ are formed under our conditions. The intercept and slope of Figure 2, obtained by the method of least squares, are $K_1 = 49 \pm 2$ and $K_1' = 500 \pm 55$ dm^3 mol^{-1}, respectively. These values can be used to calculate ε_{GaA} and ε_{GaHA}; from the results, the values of ε_C reported in the last column of Table 1 were obtained.

According to expressions (5) and (6) the ' mixed ' absorption coefficient ε_C is related to the absorption coefficients of $[GaA]^+$ and of $[Ga(HA)]^{2+}$ through relationship (8). Using

$$\varepsilon_C = \frac{\varepsilon_{GaA}K_1 + \varepsilon_{GaHA}K_1'[H^+]}{K_1 + K_1'[H^+]} \qquad (8)$$

K_1 and K_1' from our experiments we obtained a least-squares estimate of 9.8×10^3 for ε_{GaA} and 4.1×10^3 dm^3 mol^{-1} cm^{-1} for ε_{GaHA}.

Rate Constants.—Only one relaxation time was observed after the temperature jump. At any given hydrogen-ion concentration, the reciprocal relaxation times depend on the reactant concentrations according to expression (9) where

$$1/\tau = k_f([Ga_f] + [A_f]) + k_d \qquad (9)$$

k_f and k_d are the ($[H^+]$-dependent) rate constants for complex formation and decomposition, respectively. Their

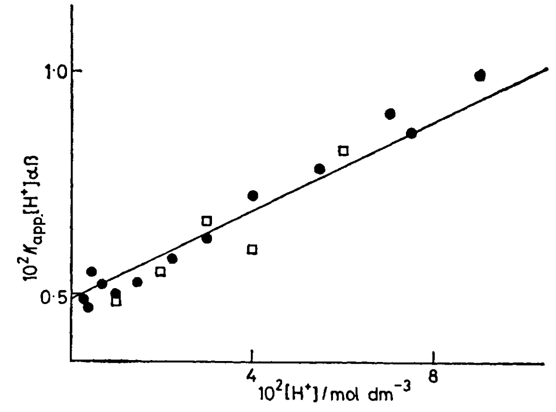
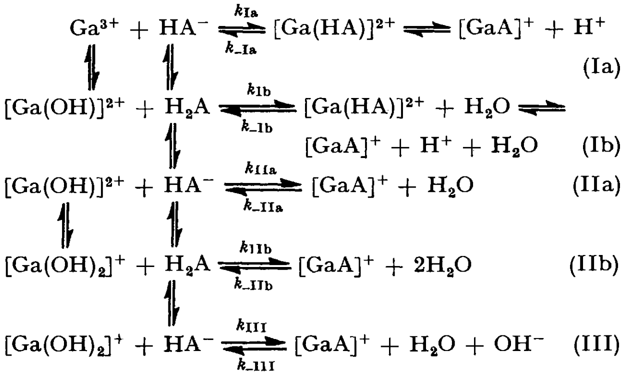


FIGURE 2 Plot of $K_{app.}\alpha\beta[H^+]$ against $[H^+]$ for spectrophotometric (●) and kinetic results (□)

ratio equals K_{app}. From the slopes and intercepts of the straight lines obtained by plotting $1/\tau$ as a function of $[Ga_f] + [A_f]$ (*ca.* c_M) values of k_f and k_d were determined at different values of $[H^+]$. Examples of these plots are shown in Figure 3. From k_f/k_d kinetic estimates of $K_{app.}$ may be obtained and these are given as squares in Figure 2. They are in good agreement with the spectrophotometric values.

On the basis of our results, we suggest the reaction scheme (I)—(III). When the loss and addition of H^+ are



$$Ga^{3+} + HA^- \underset{k_{-Ia}}{\overset{k_{Ia}}{\rightleftharpoons}} [Ga(HA)]^{2+} \rightleftharpoons [GaA]^+ + H^+ \quad (Ia)$$

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

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

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

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

assumed to be fast in comparison with complexation, this scheme leads to equations (10) and (11). {In equation (10)

$$1/\tau B = k_1[H^+] + k_2 + (k_3/[H^+]) \qquad (10)$$

$$B = \frac{([Ga_f] + [A_f])K_{app.} + 1}{K_1 + K_1'[H^+]} \qquad (11)$$

the change of $[H^+]$ during complex formation is neglected. When this is taken into account, a correction term is obtained which is always less than 1% of the corresponding B.}

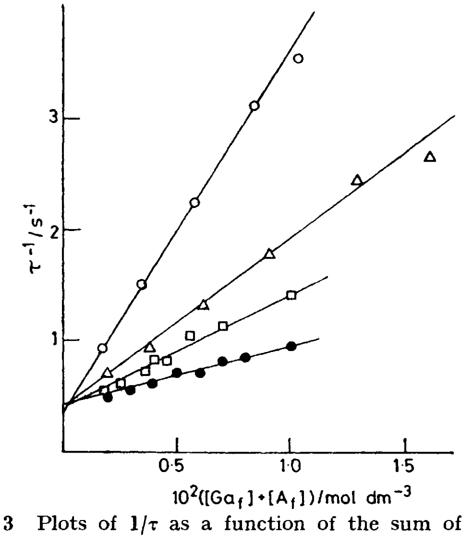


FIGURE 3 Plots of $1/\tau$ as a function of the sum of the concentrations of uncomplexed gallium and 5-nitrosalicylate ions. $[H^+] = 0.01$ (○), 0.02 (△), 0.03 (□), and 0.04 mol dm^{-3} (●)

The rate constants are defined in (12)—(14). Comparing equations (10) and (11) with (7) and (9) one can easily see that $k_f = \{k_1[H^+] + k_2 + (k_3/[H^+])\}/\alpha\beta[H^+]$.

$$k_1 = k_{Ia} + (k_{Ib}K_{H1}/K_{A1}) \qquad (12)$$

$$k_2 = k_{IIa}K_{H1} + (k_{IIb}K_{H1}K_{H2}/K_{A1}) \qquad (13)$$

$$k_3 = k_{III}K_{H1}K_{H2} \qquad (14)$$

Figure 4 shows a plot of $1/\tau B$ as a function of $[H^+]$, for 48 experiments. Treating this line as a linear regression in two variables, $[H^+]$ and $1/[H^+]$, we obtain $k_1 = (4.1 \pm 0.2) \times 10^2$ dm^3 mol^{-1} s^{-1}, $k_2 = 7.9 \pm 0.9$ s^{-1}, and $k_3 = (9.4 \pm 5.0) \times 10^{-3}$ mol dm^{-3} s^{-1}. The curve shows *no* upward trend at the highest value of $[H^+]$. We therefore have not included in our scheme a reaction involving Ga^{3+} and H_2A.

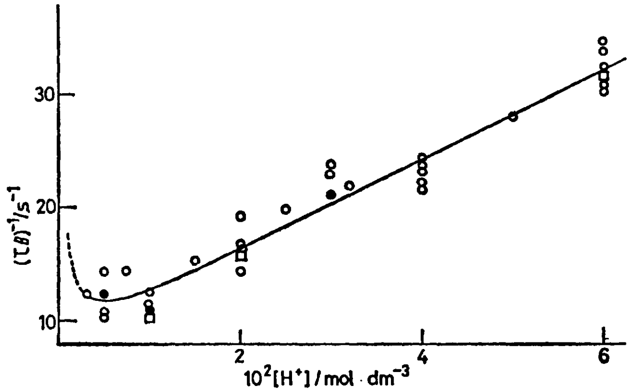


FIGURE 4 Plot of $1/\tau B$ as a function of $[H^+]$. The symbols indicate values from one (○), two (□), and three experiments (●)

DISCUSSION

Equilibrium Constants.—The reaction between the Ga^{3+} and 5-nitrosalicylate ions can be regarded as occurring first through interaction between the metal ion and the carboxylate group of the ligand, giving rise to a unidentate carboxylato-complex which in turn is converted into the chelate. The second step involves ring closure and deprotonation.

The presence of the protonated species $[Ga(HA)]^{2+}$ was not detected in our investigation of the analogous system gallium(III)-salicylate ion.[9] It should be noted, however, that in that study we had to work at an acidity of at most 10^{-2} mol dm^{-3}. At this value of $[H^+]$ the quotient $[Ga(HA)^{2+}]/[GaA^+]$ is only 0.1 in our present system. If we assume the same value also for the gallium(III)-salicylate ion system it is not surprising that the monoprotonated species escaped our attention. Non-negligible amounts of a unidentate ligand complex have been reported.[18,19]

A comparison of our K_1 with $K_1 = 15.6$ for the gallium(III)-salicylate ion system [9] shows that K_1 is higher the more acidic is the ligand. This fact, although at first sight surprising, is a consequence of the greater lability of the phenolic proton which is displaced when the complex is formed.[5]

Rate Constants.—In deriving equation (9) we have assumed equilibrium (IV) to be fast in comparison with

$$[Ga(HA)]^{2+} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [GaA]^+ + H^+ \qquad (IV)$$

the rate of formation and decomposition of the complex with unidentate ligand. Since step (IV) involves ring closure (and opening) with concomitant or subsequent deprotonation (and protonation), the possibility that this process should be rate-determining cannot be excluded

TABLE 2

Forward and reverse rate constants for different reaction paths in the gallium(III)–5-nitrosalicylate ion system and first-order rate constants for ligand penetration, k^*

Path	Metal ion	Ligand	k_i [a]/dm^3 mol^{-1} s^{-1}	k_i^0 [b]/dm^3 mol^{-1} s^{-1}	k^* [c]/s^{-1}	k_{-i} [d]
(Ia)	Ga^{3+}	HA^-	$\leqslant 4.1 \times 10^2$	$\leqslant 1.72 \times 10^3$	$\leqslant 81.2$	$\leqslant 0.81$ s^{-1}
(Ib)	$[Ga(OH)]^{2+}$	H_2A	$\leqslant 1.88 \times 10^3$	$\leqslant 1.88 \times 10^3$	$\leqslant 6.3 \times 10^3$	
(IIa)	$[Ga(OH)]^{2+}$	HA^-	$\leqslant 6.4 \times 10^3$	$\leqslant 1.67 \times 10^4$	$\leqslant 3.2 \times 10^3$	$\leqslant 0.16$ s^{-1}
(IIb)	$[Ga(OH)_2]^+$	H_2A	$\leqslant 1.7 \times 10^5$	$\leqslant 1.7 \times 10^5$	$\leqslant 5.7 \times 10^5$	
(III)	$[Ga(OH)_2]^+$	HA^-	3.6×10^4	5.9×10^4	4.5×10^4	1.21×10^{10} dm^3 mol^{-1} s^{-1}

[a] Values corresponding to paths (a) have been calculated by assuming the rates of paths (b) to be negligibly small. The opposite assumption has been made in calculating values for paths (b). [b] Values at $I = 0$, calculated with the aid of the Davies equation ($B = 0.3$). [c] Calculated from $k^* = k_i^0/K_{os}$ where K_{os} at $I = 0$ is obtained from the Fuoss equation, with $a = 5$ Å. [d] Obtained from forward rate constants and equilibrium constants.

a priori. In this case, however, the kinetic expression becomes (15) (see ref. 19) and the plots in Figure 3

$$\frac{1}{\tau} = \left(k_4K_1' + \frac{k_2K_H}{[H^+]}\right)\frac{[Ga_f] + [A_f]}{\alpha\beta + K_1'([Ga_f] + [A_f])} + k_{-4}[H^+] + k_{-2} \quad (15)$$

would display a downward curvature at the investigated acidities. In the most unfavourable case, the term $K_1'([Ga_f] + [A_f])$ is 0.1 times $\alpha\beta$, but in most cases it is actually higher than $\alpha\beta$. Since *no* curvature has been observed, the possibility of reaction (IV) being rate-determining can be ruled out.

Equations (12)—(14) show that paths (Ia) and (Ib) exhibit proton ambiguity, that is they have the same $[H^+]$ dependence. The same is true for paths (IIa) and (IIb). We therefore cannot assign definite values to the individual rate constants, but can again only estimate upper limits by assuming either of the two rate constants to be equal to zero. The results are shown in Table 2, together with the rate constants for the reverse reactions, calculated with the aid of the equilibrium constants. The extremely high value for the reaction between $[GaA]^+$ and OH^- shows that this reaction, again,[9] proceeds in two steps.

In the S_N1-ion pair mechanism the observed rate constant for the forward reaction i is given by[3] (16)

$$k_i = k^*K_{os} \quad (16)$$

where K_{os} is the stability constant of the outer-sphere complex and k^* is the reciprocal of the lifetime of a water molecule in the inner co-ordination sphere, multiplied by a statistical factor[20] of 3/4. In the penultimate column of Table 2 we present the values of k^* obtained from equation (16), using values of K_{os} derived from the Fuoss equation[21] with $a = 5$ Å, and correcting the values of k_i to zero ionic strength with the aid of the Davies equation (with $B = 0.3$). The most recent value for k^* as determined from n.m.r. measurements[22] [$7.6 \times (3/4) \times 10^2 = 5.7 \times 10^2$ s^{-1}], although lower than that previously reported,[6] is still considerably higher than that calculated from the rate of formation of our complex. Whereas this fact does not exclude the S_N1-ion pair mechanism, our result provides additional evidence[9,10] for the wide scatter of k^* calculated for Ga^{3+} from its rates of reaction with different ligands.

This scatter argues in favour of an S_N2 mechanism. Equation (16) remains valid, provided k^* is now interpreted as the rate of reaction between the reactants in the solvent cage.[23] The use of the Fuoss equation for the calculation of K_{os} ensures correction for the charge effect.

Whereas previously[9,10] we were unable to detect any correlation between k^* and the basicity of the entering ligand, such a correlation clearly exists for the two closely similar ligands salicylate and 5-nitrosalicylate ion. This is illustrated in Figure 5 where log k^* is plotted as a function of the pK_A of the conjugate acid of the entering ligand, for four ligands.[6,7,9,10]

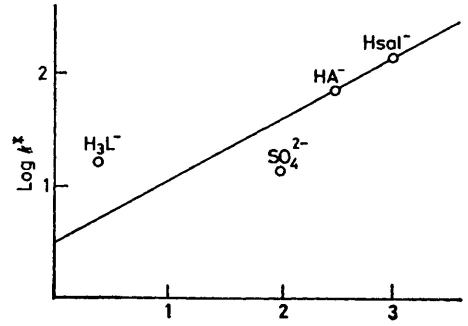


FIGURE 5 Plot of the logarithm of the first-order rate constant k^* as a function of pK_A of the entering groups $H_3L^- =$ Pyrocatechol Violet (ref. 9), $Hsal^- =$ salicylate ion (ref. 8), SO_4^{2-} (ref. 6), and HA^- (this work)

The species $[Ga(OH)_2]^+$ reacts with HA^- at least 14 times faster than $[Ga(OH)]^{2+}$, and at least 500 times faster than Ga^{3+}. This enhanced reactivity of the hydrolysed species is a feature[1-3,5] which Ga^{III} has in common with Al^{III} and Fe^{III} and which, in view of the labilising effect of OH^- on the remaining water molecules in the inner co-ordination sphere, is sometimes adduced as corroboration for the S_N1 mechanism characterised by rate-determining water loss. It does not seem evident to us, however, that a valid conclusion can be drawn on the mechanism of the *unhydrolysed* species from the reactivity of the *hydrolysed* species.[5] In the present case, this conclusion would certainly be wrong.

From a comparison with previous results,[9] it emerges that the rate constants for both hydrolysed species in our *present* system are lower than the analogous values in the salicylate ion system {except for the reaction between $[Ga(OH)]^{2+}$ and H_2A for which, in any case, only an upper limit can be given}. It should be noted that this conclusion is *unaffected* by the proton ambiguity of reactions (IIa) and (IIb), since they *both* involve hydrolysed species. This somewhat surprising ligand dependence hints at the possibility of an associative character not only for the reactions of Ga^{3+} but also for those of $[Ga(OH)]^{2+}$ and $[Ga(OH)_2]^{+}$.

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