Kinetics and Equilibria of Ga(III)–Thiocyanate Complex Formation. Mechanism of Ligand Substitution Reactions of Ga(III) in Aqueous Solution

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Abstract

The kinetics and equilibria of complex formation by Ga(III) with NCS^- in aqueous solution have been measured over a range of acidities and temperatures, the contributing paths to the reaction resolved, and their rate constants and activation parameters determined. The hydrolysis equilibria required to carry out this resolution of kinetic behaviour have also been measured.

Unlike other reported complexation reactions of Ga(III) in aqueous solution, the separate reaction pathways can be assigned with no ambiguity. At 25 °C and ionic strength 0.5 M, the observed forward rate constant for the complex formation is described by $\{k_1 + k_2K_{1h}/[H^+] + k_3K_{1h}K_{2h}/[H^+]^2\}$ M^{-1} s^{-1}. For these conditions, the first and second successive hydrolysis constants of $Ga(H_2O)_6^{3+}$ are given by $pK_{1h} = 3.69 \pm 0.01$ and $pK_{2h} = 3.74 \pm 0.04$. The rate constants corresponding to the reactions of the species $Ga(H_2O)_6^{3+}$, $Ga(H_2O)_5(OH)^{2+}$ and $Ga(H_2O)_4(OH)_2^+$ with NCS^- are $k_1 = 57 \pm 4$ M^{-1} s^{-1}, $k_2 = (1.08 \pm 0.01) \times 10^5$ M^{-1} s^{-1} and $k_3 = 3 \times 10^6$ M^{-1} s^{-1} respectively. The complexation equilibrium quotient $[GaNCS^{2+}]/([Ga^{3+}][NCS^-])$ has been independently determined by spectrophotometric titration to be 20.8 ± 0.3 M^{-1} at 25 °C and ionic strength 0.5 M.

These kinetic results lead to an interpretation of the data, and a reinterpretation of other data for aquo-Ga(III) complex formation kinetics from the literature which support the assignment of a dissociative interchange mechanism for these reactions rather than the associative activation mode sometimes proposed.

Introduction

The ligand substitution mechanism for Ga(III) complexes is by no means clear. In non-aqueous solvents the interpretation of the solvent exchange kinetics, activation enthalpies, entropies and volumes data for Ga(III) has been in terms of a dissociative or dissociative interchange mechanism, except, as also appears true for Al(III), for the case of very bulky solvent molecules, where the coordination is reduced to four and the solvent exchange activation volume data support a more associative activation [1, 2]. In water, the dependence of the kinetics of formation of a number of salicylate complexes on the basicity of the ligand has been cited to support proposals for an associative interchange mechanism of complex formation [3, 4]. This contrasts with the earlier observations of $Ga(SO_4)^+$ complex formation in water [5] which were taken to support a conventional Eigen–Wilkins I_d(IP) mechanism.

The interpretation of the observed kinetics in aqueous solution of a hydrolysable complex, such as $Ga(H_2O)_6^{3+}$, reacting with basic ligands, such as salicylate or sulphate, is complicated by the possibility of up to six parallel pathways, a number of which may have the same acid dependence. Assumptions about which of the paths gives rise to a particular observed acid dependence are central to the interpretation of the data; an incorrect assumption can lead to an erroneous assignment of the mechanism.

This complicated reaction scheme can be simplified by studying the reaction of Ga(III) with NCS^-, a ligand which is not protonated except at very high acidities. This system, therefore avoids the 'proton-ambiguity' problem of reaction of more basic ligands with hydrolysable metal ions such as Ga(III) [3], or indeed Fe(III), which has a long history of such ambiguities of interpretation [6, 7].

We have, therefore, carried out a spectrophotometric stopped flow kinetic study of the Ga(III)/NCS^- system over a range of reactant concentrations, acidities, temperatures and ionic strengths. We also report an independent equilibrium study of this system, together with new measurements of the hydrolysis equilibria associated with solutions of Ga(III) in aqueous media, which are required for the analysis of the kinetic data.

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Experimental

Materials

Stock solutions of gallium(III) perchlorate were prepared by the anodic oxidation of gallium metal (Koch-Light, 99.999% pure), in a known excess of perchloric acid (BDH, Analar). The cathode consisted of a cylindrical platinum wire mesh of large surface area which surrounded the gallium metal anode; a slight overpotential was supplied at a current of 40 mA. The concentration of Ga(III) determined by EDTA titrations using Cu(II)-EDTA and 1-(2-pyridylazo)2-naphthol as the indicator agreed with that obtained from the weight loss of the gallium metal electrode due to the oxidation. The stock solution of Ga(III) was kept acidified with perchloric acid to minimize the formation of polymeric hydrolytic species.

Stock solutions of sodium perchlorate monohydrate (Koch-Light, AR), which was used to maintain ionic strength, and oven-dried sodium thiocyanate (AJAX, Univar) were prepared by weight. Stock perchloric acid solutions were standardized by titration against borax. Sodium hydroxide solutions for the potentiometric titrations were prepared from carbonate-free ampoules (BDH) and handled in a glove box under nitrogen. Twice distilled, one deionized water was used throughout.

Apparatus

The hydrolysis constants for Ga(III) were determined by potentiometric titration using a combined glass electrode (Radiometer GK2401C), in which the reference cell saturated KCl electrolyte had been replaced by 1 M NaCl to prevent the precipitation of potassium perchlorate at the electrode liquid junction. The electrode was calibrated against a series of perchloric acid solutions of known hydrogen ion concentration at the required ionic strength; slope of the $\log[H^+]$ *vs.* electrode potential was typically 0.059 ± 0.001 V.

All titrations were performed automatically on a titrimeter controlled by a DEC PDP-11-10S minicomputer equipped with digital and analogue input and output for data collection and experiment control; titrant was delivered from a stepper motor driven syringe burette. The potentiometric titrations were controlled by a BASIC program which allowed the user to calibrate the electrode, input the experimental conditions and save the titration data on disk. Typically, 200 to 300 additions of titrant were made over a period of two to five hours. The reaction vessel, which could be thermostatted between 10 and 40 °C to ±0.2 °C, was purged with nitrogen before and during a titration.

Complexation equilibrium constants were determined by spectrophotometric titrations carried out in a themostatted 4 cm pathlength cell in a Varian 635D spectrophotometer. The titrant addition, experiment control and data collection used the same PDP-11 system as the potentiometric titrations.

Kinetic experiments were carried out using a stopped-flow instrument designed and constructed within this Department [8]; reactions were followed using optical absorbance measurements at 220 nm. The mixing time of the equipment is around 2 msec, for a 2 mm pathlength optical cell and about 8 msec for an 18 mm pathlength cell. The apparatus can be efficiently thermostatted between 7 and 40 °C to ±0.02 °C.

All stopped-flow experiments were also under PDP-11 computer control from a BASIC program which allowed the user to input the experimental conditions, select the data sampling rate, calculate pseudo-first order rate constants and save the reaction trace, together with the experimental parameters, on disk. Each run consisted of 200 data points, collected automatically using a 10 bit A/D converter at the required sampling interval, together with 20 equilibrium points obtained after a predetermined time interval. The sampling rate was usually selected so that 90% of the reaction was completed during collection of the first 200 data points. Usually around 10 experimental traces were collected under the same conditions and signal-averaged. The deviations between individual rate constants, calculated using a Guggenheim expression for data collected over four half lives, were less than 5% and deviations of less than 1% were not uncommon.

Kinetic Reaction Scheme

For the reaction of Ga(III) with thiocyanate, a kinetic expression was derived based on Reaction Scheme 1, where the coordinated water molecules have been omitted for clarity. The forward and reverse rate constants for reactions (I), (II) and (III) are k_1, k_{-1}, k_2, k_{-2}, k_3 and k_{-3} respectively. The proton transfer equilibria, K_{1h} and K_{2h}, involving successive hydrolyses of the aquo-Ga(III) species, or $K_{1hGaNCS}$ and $K_{2hGaNCS}$, involving successive hydrolyses of the thiocyanato–Ga(III) species, are assumed to be labile compared to the rates of metal–ligand complexation.

For this scheme**, it can be shown that the observed rate constant for reaction of Ga(III) with NCS^- is described by

$$k_{obs} = k_{for}\{[Ga(III)]_T + [NCS^-]_T - 3[GaNCS^{2+}]_{eq}/2\}/\delta + k_{rev} \quad (1)$$

**Full details of the derivation of this expression are available from the authors as supplementary material.

$$Ga^{3+} + NCS^- \rightleftharpoons GaNCS^{2+} \qquad k_1, k_{-1} \qquad \text{(I)}$$

$$\text{fast } +H^+ \uparrow\downarrow K_{1h} \qquad \text{fast } +H^+ \uparrow\downarrow K_{1hGaNCS}$$

$$Ga(OH)^{2+} + NCS^- \rightleftharpoons Ga(OH)NCS^+ \qquad k_2, k_{-2} \qquad \text{(II)}$$

$$\text{fast } +H^+ \uparrow\downarrow K_{2h} \qquad \text{fast } +H^+ \uparrow\downarrow K_{2hGaNCS}$$

$$Ga(OH)_2^+ + NCS^- \rightleftharpoons Ga(OH)_2(NCS) \qquad k_3, k_{-3} \qquad \text{(III)}$$

Scheme 1.

where

$$k_{for} = k_1 + k_2K_{1h}/[H^+] + k_3K_{1h}K_{2h}/[H^+]^2 \qquad (2)$$

$$k_{rev} = k_{-1} + k_{-2}K_{1hGaNCS}/[H^+] + k_{-3}K_{1hGaNCS}K_{2hGaNCS}/[H^+]^2 \qquad (3)$$

and

$$\delta = 1 + K_{1h}/[H^+] + K_{1h}K_{2h}/[H^+]^2 \qquad (4)$$

Thus a series of experiments at a given acid concentration, in which the metal concentration was varied, allowed the determination of the observed forward and reverse rate constants, k_{for} and k_{rev}, at that acidity by fitting the data to eqn. (1). Combination of this observed rate constant data at different acidities made possible the resolution of the rate constants for the individual pathways using the expressions (2), (3) and (4). Activation parameters were obtained by repeating these experiments at various temperatures.

Results

Hydrolysis Equilibria

Because of the large variation of published values of the hydrolysis constants, it was decided to re-investigate the hydrolysis of Ga(III). Potentiometric titrations were performed at 25 °C with metal ion concentrations in the range 4×10^{-4} M to 1×10^{-2} M, and at ionic strengths of 0.1, 0.5 and 1.5 M. A temperature dependence at 0.5 M ionic strength was also carried out. All Ga(III) solutions to be titrated were freshly prepared by dilution from the stock solution of Ga(III). The pH of each Ga(III) solution was then adjusted by the addition of dilute perchloric acid or sodium bicarbonate solution, so that the initial pH was about 2.

Typical titration curves for the hydrolysis of Ga(III) are shown in Fig. 1. For all 18 titrations, carried out as part of the study under various conditions, a plateau was observed at a pH between 3.0 and 3.4. In this plateau region, pH equilibrium

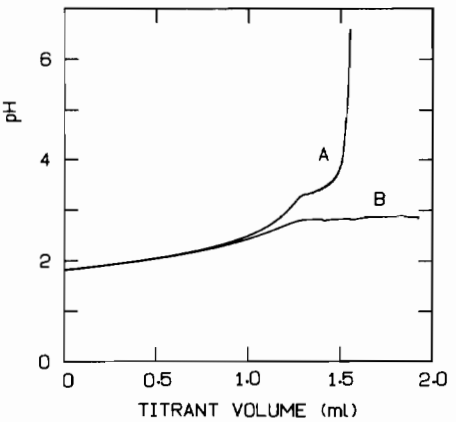


Fig. 1. Hydrolysis of aqueous gallium(III). Titration curves of solution pH *vs.* volume of NaOH titrant added (ml). Curve A: $[Ga(III)]_T = 8.38 \times 10^{-4}$ M, [titrant] = 0.01 M, temperature = 25 °C, ionic strength = 0.5 M, 229 data points. Curve B: $[Ga(III)]_T = 8.38 \times 10^{-3}$ M, [titrant] = 0.1 M, temperature = 25 °C, ionic strength = 0.5 M, 138 data points.

was always slowly attained and was sometimes unstable, presumably due to slow hydroxo polymer formation; precipitation was sometimes observed. Measurements obtained before the plateau reached pH equilibrium almost immediately after each addition of base. Increasing the metal ion concentration decreased the pH at which the plateau began, as did increasing the temperature or decreasing the ionic strength at constant metal ion concentration. Only data obtained before the plateau region were included in the analysis to determine hydrolysis constants.

The data were fitted using a version of the non-linear least squares program MINIQUAD [9] assuming the presence of the Ga(III) species Ga^{3+}, $GaOH^{2+}$ and $Ga(OH)_2^+$. These species are consistent with those assigned in kinetic pathways by several workers under similar experimental conditions [3, 4]. Attempts to fit the data to more complex schemes, involving further hydrolysis or the formation of polymeric species, usually led to non-convergence, or to results with large errors and non-random residuals. Our results are summarized

TABLE I. Summary of Hydrolysis Constant Determinations for Ga(III).

Temp. (°C)	Ionic strength (M)	pK_{1h}	pK_{2h}	Reference
10	0.5	4.17 ± 0.01	4.04 ± 0.06	this work
25	0.1	3.50 ± 0.01	4.17 ± 0.08	this work
25	0.5	3.69 ± 0.01	3.74 ± 0.04	this work
25	1.5	4.15 ± 0.04	2.82 ± 0.06	this work
18	0	2.8	3.5	[17]
20	1.0	3.6		[13]
25	0.1	2.87	3.71	[14]
25	0.5	2.30	2.91	[14]
25	1.0	1.78	2.09	[14]
25		3.28		[15]
25	various	3.34–3.43		[16]

in Table I, together with some previously reported data.

From the temperature dependences of K_{1h} and K_{2h} at 0.5 M ionic strength, ΔH values of 52 kJ mol^{-1} and 30 kJ mol^{-1} respectively were obtained.

Complexation Equilibria

The equilibrium constant for complexation of Ga(III) by thiocyanate was determined from a series of competition experiments between the $GaNCS^{2+}$ and $CuNCS^{+}$ association equilibria. The extent of association between Ga(III) and NCS^{-} was measured by observing the change in absorbance at 343 nm, the absorption maximum of the $CuNCS^{+}$ complex, upon titration of NCS^{-} into an acid solution of Ga(III) containing Cu(II) at 25 °C and I = 0.5 M, and comparing this with the absorbance of an identical series of solutions in the absence of Ga(III).

These experiments require the equilibrium constant for $Cu(NCS)^{+}$ formation and the extinction coefficient of $Cu(NCS)^{+}$ at 343 nm. These were determined from separate titrations and analysed using a Benesi–Hilderband expression to be 56.0 ± 0.2 M^{-1} and 495 cm^{-1}; this agrees well with reported values (55 M^{-1} [10], 481 cm^{-1} [11]).

From a series of experiments in which [Ga(III)] was typically 0.004 M, [Cu(II)] 0.08 M, [NCS^{-}] 0.002 M and [H^{+}] 0.01 M, assuming that formation of higher thiocyanato complexes can be neglected, K_1 defined as $[GaNCS^{2+}]/([Ga^{3+}][NCS^{-}])$ is 20.8 ± 0.3 M^{-1}. This can be compared with 15.2 M^{-1} (20 °C, I = 0.6 M) [12] and our independent kinetic determination of 21 M^{-1}.

Complexation Kinetics

For these experiments, [Ga(III)] was varied in the range 0.001 M to 0.035 M, [NCS^{-}] was 0.0017 M to 0.0019 M, and the acid concentration varied from 0.01 M to 3 M. The extent of complexation was small and pseudo-first order kinetics were always observed. Ionic strength was maintained at 0.5 M except at the highest acidities, when the ionic strength was dominated by this high acidity.

Plots to determine k_{for} and k_{rev} at 25 °C at various acid concentrations using expression (1) are together with those from similar experiments at 18 °C, 12 °C and 7 °C is available†. The minor correction term involving $[GaNCS^{2+}]_{eq}$ in expression (1) was calculated iteratively using the equilibrium constant

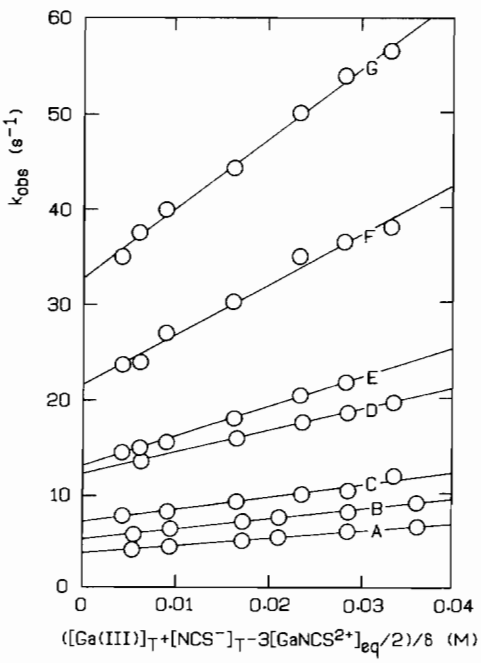


Fig. 2. Complexation kinetics of Ga(III) by SCN^{-} at 25 °C. k_{obs} (s^{-1}) *vs.* $\{[Ga(III)]_T + [NCS^{-}]_T - 3[GaNCS^{2+}]_{eq}/2\}/\delta$ (M). Data at a variety of [H^{+}]: A 1.505 M, B 0.530 M, C 0.316 M, D 0.130 M, E 0.094 M, F 0.053 M, G 0.0375 M.

†These data are available from the authors as supplementary material.

given by the ratio k_{for}/k_{rev}; convergence to within 0.1% for this ratio was usually obtained within three or four iterations. The equilibrium constant obtained in this way was found to be independent of $[H^+]$ and temperature with a mean value 21 ± 2 M^{-1}.

A plot of k_{for} at 25 °C as a function of $1/[H^+]$ is shown in Fig. 3; analogous plots were obtained

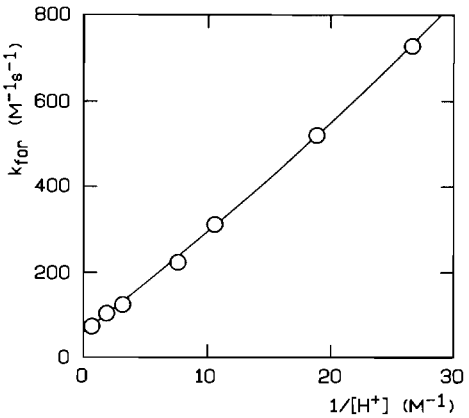


Fig. 3. Acid dependence of complexation kinetics of Ga(III) by SCN^- at 25 °C. k_{for} (M^{-1} s^{-1}) *vs.* $1/[H^+]$ (M^{-1}).

at 18 °C, 12 °C and 7 °C. A least squares fit to expression (2) was used to resolve the rate constants for paths (I), (II) and (III) using the values of K_{1h} and K_{2h} reported above. These values are summarized in Table II. For the data at 25 °C and 18 °C it was felt that the precision of the data justified the use of the full quadratic expression (2). For the lower temperature data, however, the curvature attributed to the reaction path involving $Ga(OH)_2^{2+}$ was not observed, due primarily, we would suggest, to the decreased concentration of $Ga(OH)_2^{2+}$ at lower temperatures. If the lowest acid point at each of 18 °C and 25 °C, which are the data showing the largest contribution from the proposed path (3), is neglected, and only the acid independent and $1/[H^+]$ terms of expression (2) assumed, values determined for k_1 and k_2 are changed by only a few percent as shown in Table II.

As has been pointed out, to achieve higher acidities and so minimise the error in the calculation of the acid independent intercept term in plots such as Fig. 3, the ionic strength of solutions with $[H^+]$ above 0.3 M was greater than 0.5 M. Values of k_{for} were obtained at several ionic strengths and acidities; the extrapolated values of k_1 in all cases agreed to within experimental error.

A plot of k_{rev} at 25 °C as a function of $1/[H^+]$ is given in Fig. 4. The data calculated for the separate pathways from this and analogous data at other temperatures is included in Table II. This data provides another estimate of K_1, 23 M^{-1}, from k_1/k_{-1}.

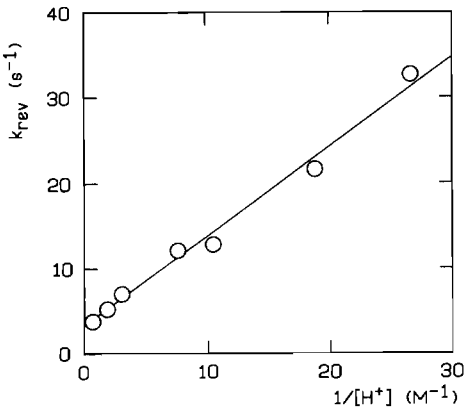


Fig. 4. Acid dependence of complexation kinetics of Ga(III) by SCN^- at 25 °C. k_{rev} (s^{-1}) *vs.* $1/[H^+]$ (M^{-1}).

TABLE II. Rate Constants for the Separate Complexation Pathways of Ga(III).

		25 °C	18 °C	12 °C	7 °C
k_1 (M^{-1} s^{-1})	a	55 ± 6	35 ± 1	19 ± 1	8.6 ± 0.8
k_2K_{1h} (s^{-1})	a	23 ± 1	7.6 ± 0.1	3.25 ± 0.05	1.90 ± 0.04
$K_{1h} \times 10^4$ (M)	b	2.04	1.24	0.79	0.53
$k_2 \times 10^{-4}$ (M^{-1} s^{-1})	a	11.3	6.1	4.1	3.6
k_1 (M^{-1} s^{-1})	c	57 ± 4	37 ± 2		
k_2K_{1h} (s^{-1})	c	22 ± 2	6.9 ± 0.6		
$k_2 \times 10^{-4}$ (M^{-1} s^{-1})	c	10.8	5.6		
$k_3K_{1h}K_{2h}$ (M s^{-1})	c	0.1	0.04		
$K_{2h} \times 10^4$ (M)	b	1.8	1.3		
$k_3 \times 10^{-6}$ (M^{-1} s^{-1})	c	2.7	2.5		
k_{-1} (s^{-1})		3.1 ± 0.7	1.5 ± 0.1	0.6 ± 0.1	0.46 ± 0.03
$k_{-2}K_{1hGaNCS}$ (M s^{-1})		1.06 ± 0.05	0.38 ± 0.01	0.19 ± 0.005	0.079 ± 0.002
k_1/k_{-1} (M^{-1})		18	25	31	19

[a]By linear fit to k_{obs} *vs.* $1/[H^+]$ as described in the text. [b]This work; interpolation of data in Table I to 18 °C. [c]By quadratic fit to k_{obs} *vs.* $1/[H^+]$.

The activation parameters for paths 1, 2 and −1, determined from the temperature dependence of k_1, k_2 and k_{-1}, are $\Delta H_1^* = 70 \pm 8$ kJ mol^{-1}, $\Delta S_1^* = 24 \pm 20$ J K^{-1} mol^{-1}, $\Delta H_2^* = 43 \pm 7$ kJ mol^{-1}, $\Delta S_2^* = -7 \pm 24$ J K^{-1} mol^{-1}, $\Delta H_{-1}^* = 77 \pm 8$ kJ mol^{-1}, $\Delta S_{-1}^* = 23 \pm 20$ J K^{-1} mol^{-1}.

Discussion

Hydrolysis Equilibria

Analysis of the hydrolysis of Ga(III) has proved a difficult system; there is a large variation in the published values of the hydrolysis constants, which have generally been obtained using indirect methods [13–17]. Models to correlate the trend of hydrolysis for aquo-cations have recently been presented by Biedermann [18], for group(III) ions using a simple electronegativity correlation, and by Barnum [19], for a much wider range of cations using a more sophisticated empirical approach also based largely on electronegativity values of the cation. While these models account in general terms for the order of pK_{1h} for the group(III) aquo-cations, Al(III) > In(III) > Ga(III) > Tl(III), which is not that expected from simple charge/radius arguments, an aspect of both of these models is the poor fit of the Ga(III) results. This is specifically pointed out by Barnum [19].

Our measured values of pK_{1h} for Ga(III) are higher than most reported; the same is true for pK_{2h}. Our new value for K_{1h} fits both the Bidermann [18] and Barnum [19] models extremely well.

Though no ΔH has been reported for the formation of $GaOH^{2+}$, the enthalpy obtained, 52 kJ mol^{-1}, is similar to that reported for the first hydrolysis step of many other metal ions, regardless of their oxidation state [20]; these values are always positive and near the enthalpy of dissociation of water (55 kJ mol^{-1}). For the formation of each successive mononuclear complex, the limited data available [20] suggest that the enthalpy of reaction decreases with each step; this is also observed in our data.

For the first and second hydrolysis processes, results obtained at various ionic strengths produced good linear plots of $-\log(K)$ *vs.* ionic strength (M). For pK_{1h} and pK_{2h} the intercepts of these plots, corresponding to the limiting pK_h at zero ionic strength, were 3.46 ± 0.002 and 4.24 ± 0.03 respectively; the slopes were 0.458 ± 0.002 M^{-1} and −0.95 ± 0.03 M^{-1}. These results were used to interpolate the hydrolysis constants to intermediate ionic strengths where required.

Complexation Equilibria and Kinetics

The rate constants for the reaction of Ga(III) with SCN^- listed in Table II are the first reported which can be unambiguously assigned to the ligand substitution reactions of $Ga(H_2O)_6^{3+}$, $Ga(H_2O)_5(OH)^{2+}$ and, we believe, $Ga(H_2O)_4(OH)_2^+$.

Secco *et al.* [3, 4] in their studies of various salicylate complexes of Ga(III) have argued for an associative interchange mechanism for ligand substitution, based on the apparent dependence of the complexation rate constant on the nature of entering group. On the basis of this proposed [4] dependence on the pK_a of the complexing ligand, it would be expected that the value of k_1 for complexation of $Ga(H_2O)_6^{3+}$ by NCS^-, with a reported pK_a of −1.84 [23], should be around 0.4 M^{-1} s^{-1}; this is in marked contrast to our measurement of 57 M^{-1} s^{-1}. Another study which does not fit this dependence on pK_a is the Ga(III)/pyrocatechol–violet system [24]. These results are shown in Fig. 5.

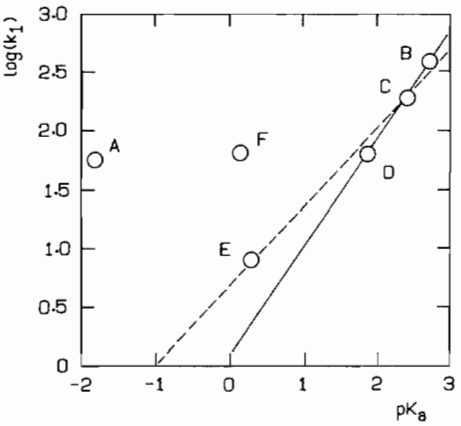


Fig. 5. Dependence of the rate constant for substitution at Ga^{3+} on the nature of the complexing ligand. $\log(k_1)$ *vs.* pK_a. A = NCS^-, B = salicylate, Sal^-, C = 5-chlorosalicylate, $ClSal^-$, D = 5-nitrosalicylate, NO_2Sal^-, E = 3,5-dinitrosalicylate, $(NO_2)_2Sal^-$, F = pyrocatechol-violet, PCV^-. Temperature 25 °C; ionic strength 0.5 M for A, 0.2 M for B–F. - - - = correlation of reference [4] using data B, C, D and E; slope 0.67 ± 0.06. —— = correlation using data for B, C and D only; slope 0.92 ± 0.05.

Another curious aspect of the salicylate substitution data is the acceleration in rate for the proposed reaction of $GaOH^{2+}$ with these anions. For other hydrolysable cations such as $Cr(H_2O)_6^{3+}$, $Fe(H_2O)_6^{3+}$ or $Al(H_2O)_6^{3+}$, the monohydroxo cation, $M(H_2O)_5(OH)^{2+}$, is typically 1200 [21], 900 [6] or 1100 [22] times more labile than the aquo species $M(H_2O)_6^{3+}$. The data proposed for the Ga(III)-salicylates suggests an increase in lability of around 25. Our results for thiocyanate complex formation give $k_1/k_2 = 1900$, which seems more in keeping with the other metal ion systems.

While our value of k_1 can be unambiguously assigned, the salicylates are examples of basic ligands for which the kinetics have a 'proton ambiguity'

[3, 6, 7]; that is, there are alternative reaction pathways which have the same acid dependence and may therefore be consistent with the experimentally observed kinetics. In Reaction Scheme 2 we have generalized our Scheme 1 to include these basic ligands.

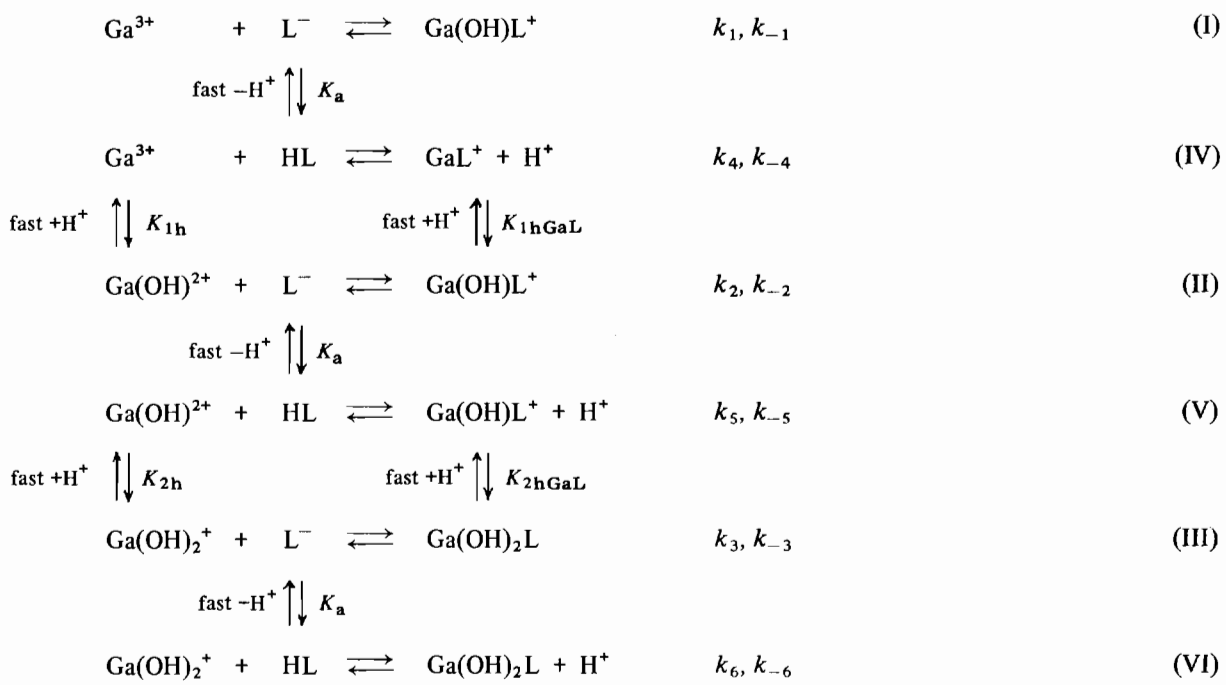
The expression for the observed forward rate constant for Scheme 1, eqn. (2), must be expanded to include four acid dependent terms:

$$k_{for} = (k_4/K_a)[H^+]^1 + (k_1 + k_5K_{1h}/K_a)[H^+]^0 + (k_2K_{1h} + k_6K_{1h}K_{2h}/K_a)[H^+]^{-1} + (k_3K_{1h}K_{2h})[H^+]^{-2} \quad (5)$$

So that for Scheme 2, the $[H^+]^0$ and $[H^+]^{-1}$ terms have coefficients which may be assigned to one of two possible paths or combinations of those alternative paths.

In Table III we have set out our measurements with those for the other Ga(III) systems reported and some assignments based on the assumption that the coefficients in eqn. (5) are associated entirely with one or the other of the possible paths. For the thiocyanate system, the value of k_6 of around 10^{11} M^{-1} s^{-1} is beyond the diffusion controlled limit, and must be dismissed in favour of the k_2 alternative, 1.1×10^5 M^{-1} s^{-1}; given this, the value of k_5, 2.0×10^7 M^{-1} s^{-1}, would suggest that the reaction of $GaOH^{2+}$ was much faster with HNCS than that with NCS^-, given by k_2, so this can also be dismissed in favour of the path given by k_1. The pyrocatecholviolet results [24], assigned in the same way, are in good agreement with the thiocyanate, giving k_1 and k_2 values of 65 and 3.8 $\times 10^4$ M^{-1} s^{-1} respectively, and would support an I_d mechanism for the interchange of the entering ligand and water, preceded by diffusion controlled outer sphere complex formation for both the Ga^{3+} and $GaOH^{2+}$ reactions. For such a mechanism, where the ligand concentration is low, the second order rate constant for complex formation will be given by $K_{OS}k_{int}$, where K_{OS} is the equilibrium constant for outer sphere complex formation and k_{int} is the rate constant for interchange of the leaving and entering ligands [25]. Using the Eigen–Fuoss equation [25] with a contact distance of 5 Å, and the Davies equation [26] to estimate the activity coefficient correction at the appropriate ionic strength, the values of K_{OS} for the Ga^{3+}/NCS^- and Ga^{3+}/PCV^- systems will be 7.5 M^{-1} and 8.8 M^{-1}, giving interchange rate constants of 7.6 s^{-1} and 7.4 s^{-1} respectively. These compare well with the k_{int} value of 5 ± 2 s^{-1} for the Ga^{3+}/SO_4^{2-} reaction [5].

For the salicylate systems, the assignment decision is not as clear cut. We would argue that the assignment of the $[H^+]^0$ coefficient to path(V) rather than to path(I) gives values which are more consistent with this work and other studies. The values of k_5, especially for HSal, HClSal and $H(NO_2)$Sal, are very constant and somewhat lower than the NCS^- and PCV^- values for k_2, in keeping with the factor of 10 difference expected on the basis of the calculated K_{OS} for $GaOH^{2+}$/HL compared



Scheme 2.

TABLE III. Rate Constants for the Alternative Complexation Pathways of Ga(III).

Ligand	Ga(III) species + L^-			Ga(III) species + HL			Ref.
	k_1 $M^{-1}\,s^{-1}$	k_2 $M^{-1}\,s^{-1}$	k_3 $M^{-1}\,s^{-1}$	k_4 $M^{-1}\,s^{-1}$	k_5 $M^{-1}\,s^{-1}$	k_6 $M^{-1}\,s^{-1}$	
NCS^-	57	1.1×10^5	3×10^6				this work
HNCS					(2.0×10^7)	(8.7×10^{10})[d]	this work
Sal^-	(392)	(7.0×10^3)					[4][a]
HSal					2.7×10^3	1.1×10^6	[4][b]
$ClSal^-$	(185)	(4.3×10^3)					[4][a]
HClSal					2.6×10^3	1.4×10^6	[4][b]
NO_2Sal^-	(63)	(2.1×10^3)					[4][a]
HNO_2Sal					3.0×10^3	2.4×10^6	[4][b]
$(NO_2)_2Sal^-$	(8.0)	(1.9×10^2)					[4][a]
$H(NO_2)_2Sal$					(1.5×10^4)	(8.5×10^6)	[4][b]
PCV^-	65	8.7×10^3					[23][a]
PCV^-	65	3.8×10^4			(1.7×10^5)	(3.1×10^8)	[23][c]
$(NO_2)_2Sal^-$	6.5	1.2×10^3					[4][e]
$H(NO_2)_2Sal$					2.8×10^3	1.6×10^6	[4][e]

[a]Assignment and values as reported in reference; $[H^+]^0$ coefficient is assigned entirely to path 1, $[H^+]^{-1}$ coefficient to path 2. [b]Alternative assignment to that presented in reference; $[H^+]^0$ coefficient is assigned entirely to path 5, $[H^+]^{-1}$ coefficient to path 6. In addition, for consistency with our own data, the data from reference [4] has been recalculated using the hydrolysis constants for Ga(III) reported in this work interpolated to 0.2 M ionic strength, 2.81×10^{-4} M. [c]Pathway assignment as presented in reference [23], but recalculated using the Ga(III) hydrolysis constants reported in this work interpolated to 0.2 M ionic strength. [d]All values given in parentheses are for assignment alternatives which are not preferred for reasons given in the text. [e]Assumes contributions from both possible pathways to the $[H^+]^0$ and $[H^+]^{-1}$ dependence coefficients and uses the hydrolysis results of this work as in b and c to calculate the rate constants.

to $GaOH^{2+}/L^-$. Indeed the constancy of these values corresponds to the slope of the $\log(k_1)$ *vs.* pK_a plot being 1, as is shown in Fig. 5, and which was pointed out [4] as evidence which would support the path(V) assignment; that this slope is given [4] as less than 1 seems to rest entirely on the dinitrosalicylate data. Assigning the $[H^+]^{-1}$ coefficient to path(VI) also gives values which are quite constant and in keeping with our result for k_3, in which the substitution takes place via the $Ga(OH)_2^+$ complex.

The assignments just described make the assumption that the $[H^+]^0$ coefficient can be assigned entirely to path(I) or to path(V), and the $[H^+]^{-1}$ to path(II) or to path(VI). In other words, the NCS^- and PCV^- react entirely via the anionic ligand and the salicylates via the protonated ligand. We would argue that there is no need to invoke a dependence of the substitution rate on the nature of the entering group and that an I_d/IP mechanism adequately describes the reaction of all Ga(III) species in aqueous solution. There is, therefore, a slight concern that of the salicylates the rate constants k_5 and k_6 for the dinitrosalicylate are measurably higher than would be expected for an I_d mechanism involving such similar ligands. We propose that for this ligand, significant amounts of reaction take place via both the anionic and protonated species. Assuming k_5 to be 2.8×10^3 $M^{-1}\,s^{-1}$, the mean of the other three salicylates, the acid independent coefficient can be partitioned to give $k_1 = 6.5$ $M^{-1}\,s^{-1}$. Similarly assuming k_6 to be 1.6×10^6 $M^{-1}\,s^{-1}$, k_2 is calculated to be 1.2×10^3 $M^{-1}\,s^{-1}$. For both these acid dependent terms then, the proportions of reaction via the anionic $(NO_2)_2Sal^-$ and the protonated $(NO_2)_2SalH$ species are virtually identical—reaction via path(I)/path(V) = path(II)/path(VI) = 80/20. If these values of k_1 and k_2 are typical of all the salicylates, the nitrosalicylate values for k_5 and k_6 would be reduced by 10% while the other salicylates would be changed by lesser amounts. This would make the salicylate data even more consistent with an I_d/IP mechanism for path(V) and path(VI).

The difference between the significantly lower value of k_1 estimated for $(NO_2)_2Sal^-$ on one hand and the k_1 values for NCS^- and PCV^- on the other, where all are singly charged anionic species, requires comment; a difference is also observed in the k_2 values for these ligands. Such differences have been reported in other reactions where a complexing ligand may be involved in internal H-bonding; in particular it has been reported [27] that for Ni(II), where the mechanism of complex formation is accepted [25] as I_d/IP, the formation of salicylate complexes is significantly slower than other Ni(II)-carboxylates, although it has been suggested [28] that other interpretations of the acid dependent kinetics do not necessarily lead to this conclusion.

In aqueous solution no generally accepted rate constant data for the solvent exchange process on Ga(III) is available because the contributions of hydrolytic species have not adequately been taken into account [29]; a similar problem existed until recently for Fe(III) [30, 31]. The data for Ga(III) complexation is limited and the decision about mechanism is equivocal; we believe the balance to be in favour of an ion pair dissociative interchange. A valuable aid in the discussion of reaction mechanism in recent years has been the determination of activation volumes for both the complexation and solvent exchange reactions of metal ions [2]. The use of high pressure methods as a probe to these Ga(III) reactions would be extremely useful.

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