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Mechanism of Complex Formation: Kinetics and Equilibria of the Gallium(III)-Pyrocatechol Violet System

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The kinetics and equilibria of the reaction between Ga(III) and pyrocatechol violet (PCV) have been investigated in aqueous solution within an $[H^+]$ range between 0.01 and 0.2 M. Absorbance data show that two complexes, respectively 1:1 and 2:1 of Ga(III) to PCV, are formed under the experimental conditions of this work. Formation of the complex GaH_2L^+ from Ga^{3+} and PCV in the form H_3L^- involves loss of one proton whereas formation of Ga_2L^{2+} involves loss of three protons. The values of the first dissociation constant of PCV and the formation constants of the 1:1 and 2:1 complexes have been evaluated by computer analysis of spectral data. The values at 25 °C and $I = 0.2$ M are respectively $Q_A = 0.72 \pm 0.02$ M, $Q_{11} = 88 \pm 8$, and $Q_{21} = 5.5 \pm 0.5$ M. The kinetic experiments were carried out by the stopped-flow technique. The results are interpreted in terms of two parallel reaction paths involving reactions of H_3L^- with Ga^{3+} and $GaOH^{2+}$. The rate constant of the pathway via Ga^{3+} and H_3L^- has a much lower constant ($k_{IA} = 65 \pm 9$ M^{-1} s^{-1}) than the rate constant of the pathway via $GaOH^{2+}$ and H_3L^- ($k_{IIA} = (8.7 \pm 0.4) \times 10^3$ M^{-1} s^{-1}), confirming the enhanced reactivity of the hydrolyzed cation. The activation parameters have been determined. The deviations from the Eigen mechanism are discussed.

Introduction

The kinetics of formation of labile complexes have been interpreted in most cases by the dissociative S_N1_{ip} mechanism,[1] according to which the observed rate constant equals $K_{os}k^*$, where K_{os} is the association constant of an outer-sphere complex and k^* is the rate of exit of a solvent molecule from the inner coordination shell of the metal ion. This picture holds for the majority of complex formation reactions of divalent cations, whereas the kinetic features of reactions of formation of labile complexes of trivalent cations are far less clear-cut. This is due to the strong hydrolysis of these ions that introduces, at the usual acidities and ionic strengths, additional paths involving reactive hydrolyzed forms which make the kinetic pattern more complicated. Possibility of polymerization further increases the difficulty of interpretation of the results.

This study of the gallium(III)-pyrocatechol violet system is an attempt of getting more light on the mechanism of formation of complexes of gallium(III) which, from previous experiments,[2-5] seems to deviate from the dissociative model at least as far as the unhydrolyzed form of the cation is concerned.

Experimental Section

Materials. An acidified stock solution of gallium perchlorate was prepared by anodic dissolution of a sample of pure metal in diluted perchloric acid. The cathode was made by a plate of smooth platinum with an area of about 4 cm^2. The intensity of the current was kept constant at 0.05 A. Since Joule effects produced the fusion of gallium, this was kept in a small container immersed in the electrolytic cell and the electrical contact was ensured by a platinum wire plunged into the fused mass of the metal. The amount of dissolved gallium was determined by weight. The title of the stock solution of gallium perchlorate was then checked by EDTA titration using PAN as an indicator[6] and found to agree exactly with the electrogravimetric determination.

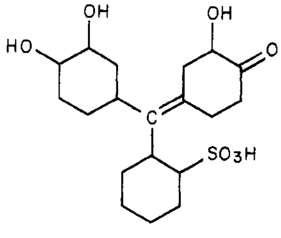
Pyrocatechol violet (3,3′,4′-trihydroxyfuchsone-2″-sulfonic acid or PCV) was Erba RP, and its purity was checked by thin-layer chromatography. Stock solutions 10^{-3} M were prepared weekly. Other chemicals were of analytical grade and their stock solutions were made in twice distilled water which was also used as a reaction medium.

Instruments. The acid content of the solutions was measured, when necessary, with a digital pH meter having an accuracy of ±0.005 pH unit. The instrument was equipped with a combined glass electrode calibrated to give directly $-\log [H^+]$. All spectrophotometric measurements were performed with a Perkin-Elmer 200 spectrophotometer. In the experiments designed to obtain the stability quotients the concentration of gallium perchlorate was always kept in excess with respect to the concentration of PCV. The required $[H^+]$ and ionic strength were obtained by addition of perchloric acid and sodium perchlorate in suitable amounts.

A Durrum-Gibson stopped-flow instrument was used to carry out the kinetic experiments. The concentration of gallium perchlorate was at least 10 times that of PCV which was, in turn, present in amounts ranging between 1 and 10×10^{-5} M. The spread between replicate runs was within 10%. The temperature fluctuations were within ±0.1 °C throughout.

Results

Equilibrium Measurements. At pH <5 PCV, whose formula is



behaves as a monoprotic acid with an equilibrium quotient, Q_A, given by eq 1. The yellow anion, H_3L^-, is predominant

$$Q_A = [H_3L^-][H^+]/[H_4L] \qquad (1)$$

between pH 2 and 5 and has a maximum absorption at 440 nm. This is shown in Figure 1 where the spectrum of PCV at pH 3 is given as a dotted-dash line. When the solution is made highly acid, a band with maximum absorbance at 555 nm (not shown in the figure) appears. This is due to the red neutral molecule, H_4L. Q_A was determined by absorbance measurements at 555 nm. Increasing amounts of perchloric acid were added by a microsyringe to solutions of PCV of concentration C_L. With the assumption that the absorbing species obey the Beer law, eq 1 and the mass conservation equation yield the relationship between absorbance, A, and $[H^+]$ in the form of eq 2, where "d" is the cell path and ϵ_{H_4L}

$$\frac{1}{(A/dC_L) - \epsilon_{H_3L}} = \frac{1}{\epsilon_{H_4L} - \epsilon_{H_3L}} + \frac{Q_A}{\epsilon_{H_4L} - \epsilon_{H_3L}} \frac{1}{[H^+]} \qquad (2)$$

and ϵ_{H_3L} are the molar absorption coefficients of H_4L and H_3L^-, respectively. ϵ_{H_3L} is known from independent measurements. An iterative weighed least-squares method[7] was used to fit 25 data points to the model represented by eq 2. The weights were assessed by setting an error of 0.002 in transmittance and an error of 0.001 mL in the volumes. The final value of the equilibrium quotient at 25 °C and $I = 0.2$ M ($NaClO_4$) is $Q_A = 0.72 \pm 0.02$ M whereas at 25 °C and $I = 1$ M (NaCl) $Q_A = 0.818 \pm 0.001$ M. From measurements of Q_A between 18.3 and 35 °C, a slight change of this quantity

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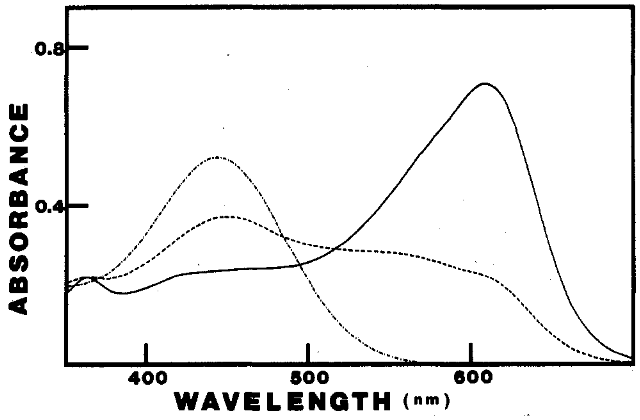

Figure 1. Spectra at pH 3 of (-·-·-) pyrocatechol violet (PCV) 3×10^{-5} M in the form of H_3L^-, (---) PCV and $Ga(ClO_4)_3$ both 3×10^{-5} M, and (—) PCV 3×10^{-5} M and $Ga(ClO_4)_3$ 10^{-4} M.

with temperature was found ($Q_A = 0.26 \exp(339/T)$ M).

When gallium perchlorate is added to a solution of PCV, a sudden change of color is indicative of the formation of complexes. The extent of complexation increases with pH, meaning that protons are lost in this process. At pH 0 no presence of complexes is detected. The spectrum represented as a dashed line in Figure 1 has been obtained with equimolar concentrations of $Ga(ClO_4)_3$ and PCV. The broad shoulder between 500 and 600 nm is ascribed to a complex of composition GaL. The continuous line represents a spectrum in the presence of excess gallium perchlorate. The band with maximum absorbance at 610 nm is due to the presence of a complex Ga_2L. At pH values between 4 and 5 a new intense band with maximum absorbance at 580 nm appears when concentrations of PCV exceed that of gallium(III). From mole ratio plots at pH 4, we inferred that this is due to formation of a species with molar composition GaL_2. Since our experiments have never been done at pH >3 nor with excess PCV, we can safely exclude the presence of GaL_2 species in the solutions and consider only the two complexes GaL and Ga_2L.

At a given constant acidity the system can be described by

$$\beta_{11} = [GaL]/[Ga_f][L_f] \tag{3}$$

$$\beta_{21} = [Ga_2L]/[Ga_f]^2[L_f] \tag{4}$$

where

$$[Ga_f] = [Ga^{3+}]\left(1 + \frac{Q_{H1}}{[H^+]} + \frac{Q_{H1}Q_{H2}}{[H^+]^2}\right) = [Ga^{3+}]\gamma \tag{5}$$

$$[L_f] = [H_3L^-](1 + [H^+]/Q_A) = [H_3L^-]\alpha \tag{6}$$

$Q_{H1} = 1.23 \times 10^{-3}$ M and $Q_{H2} = 2.01 \times 10^{-4}$ M are respectively the first and second acidity constants of Ga^{3+} ion.[9] β_{11} and β_{21} are apparent constants which depend on pH. In addition eq 7 must hold.[8] Introduction of eq 3–6 and mass

$$A = \epsilon_L[L_f] + \epsilon_{GaL}[GaL] + \epsilon_{Ga_2L}[Ga_2L] \tag{7}$$

conservation equations into eq 7 gives

$$\frac{A}{dC_L} = \frac{\epsilon_L + \epsilon_{GaL}\beta_{11}C_M + \epsilon_{Ga_2L}\beta_{21}C_M^2}{1 + \beta_{11}C_M + \beta_{21}C_M^2} \tag{8}$$

provided that the analytical concentration of gallium(III), C_M, is in excess with respect to C_L.

The above-mentioned iterative least-squares procedure[7] was applied to the nonlinear equation (8) and values of the parameters were evaluated at different hydrogen ion concentrations. The results are summarized in Table I where β_{11} and β_{21} are reported as mean values of measurements performed at 440 and 555 nm. Both the apparent stability quotients increase with pH, but β_{21} changes much more sharply than β_{11}. At $[H^+] > 0.01$ M the values of β_{21} become unreliable. A picture in satisfactory agreement with the acidity dependence of β_{11} and β_{21} is given by the reactions

Table I. Values of Apparent Stability Constants β_{11} and β_{21} for the Gallium(III)–Pyrocatechol Violet System at 25 °C and Ionic Strength 0.1 M ($NaClO_4$)

$10^2[H^+]$/M	$10^{-3}\beta_{11}{}^b$/M^{-1}	$10^{-7}\beta_{21}{}^b$/M^{-2}
0.2	23.5 ± 0.6	31.7 ± 0.4
0.5	18.6 ± 0.1	3.39 ± 0.08
0.8	12.7 ± 0.1	0.74 ± 0.05
1.0	10.2 ± 0.1	0.45 ± 0.03
3.0	3.39 ± 0.01	
6.0	1.60 ± 0.00	
8.0	1.24 ± 0.01	
10	0.886 ± 0.010	
15[a]	0.426 ± 0.040	
20[a]	0.335 ± 0.007	

[a] Ionic strengths are 0.15 and 0.2, respectively. [b] Mean values of measurements at 440 and 555 nm.

$$Ga^{3+} + H_3L^- \rightleftharpoons GaH_2L^+ + H^+ \tag{9}$$

$$2Ga^{3+} + H_3L^- \rightleftharpoons Ga_2L^{2+} + 3H^+ \tag{10}$$

with the equilibrium quotients

$$Q_{11} = [GaH_2L^+][H^+]/[Ga^{3+}][H_3L^-] \tag{11}$$

$$Q_{21} = [Ga_2L^{2+}][H^+]^3/[Ga^{3+}]^2[H_3L^-] \tag{12}$$

Introduction of eq 3, 5, and 6 into eq 11 yields

$$\beta_{11}\alpha\gamma = Q_{11}/[H^+] \tag{13}$$

and introduction of eq 4–6 into eq 11 yields

$$\beta_{21}\alpha\gamma^2 = Q_{21}/[H^+]^3 \tag{14}$$

A plot of the left-hand side of eq 13 against $1/[H^+]$ gives a straight line with slope $Q_{11} = 100 \pm 16$ at 25 °C and ionic strength 0.1 M. Similarly $Q_{21} = 5.5 \pm 0.5$ M. Values of β_{11} were also obtained at 18.3, 25, 30, 35, and 40 °C and ionic strength 0.2 M. For each temperature, three experiments at $[H^+] = 0.1$, 0.15, and 0.2 M were carried out. At these acidities we can set $\gamma = 1$ and overcome the difficulty introduced by the fact that values of Q_{H1} and Q_{H2} at temperatures other than 25 °C are not available. In Figure 2 is shown a plot of $\beta_{11}\alpha$ against $1/[H^+]$. Since β_{11} was found to be independent of the temperature, the mean values of determinations performed at the above-mentioned temperatures were used to obtain the data represented as circles. These are fitted, according to eq 13, by a straight line with zero intercept and with slope $Q_{11} = 88 \pm 8$.

Rate Measurements. Kinetic runs have been carried out with $C_M \gg C_L$ except when the decomposition of the complex was investigated. The hydrogen ion concentrations were such that $[GaL] > [Ga_2L]$ in most cases. At the lowest acidities (0.01 M) significant amounts of the dinuclear complex are formed. However, we have found the equilibrium between GaL and Ga_2L to be fast in comparison with eq 3, and therefore only the reaction

$$Ga_f + L_f \underset{k_d}{\overset{k_f}{\rightleftharpoons}} GaL \tag{15}$$

contributes to the observed kinetics.[10]

The pseudo-first-order rate constants, k_{obsd}, obtained from plots of log $(A_\infty - A)$ against time are independent of the initial concentrations of PCV whereas they increase linearly with concentrations of gallium(III) as shown in Figure 3. At constant $[H^+]$ we can write

$$k_{obsd} = k_fC_M + k_d \tag{16}$$

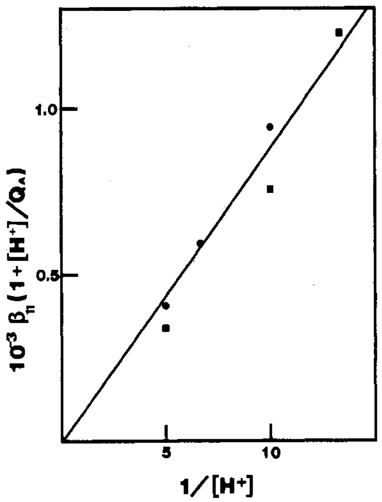

Figure 2. Plots of $\beta_{11}\alpha$ against $1/[H^+]$ for the reaction between gallium(III) and pyrocatechol violet at $I = 0.2$ M: ●, spectrophotometric results; ■, kinetic results at 25 °C.

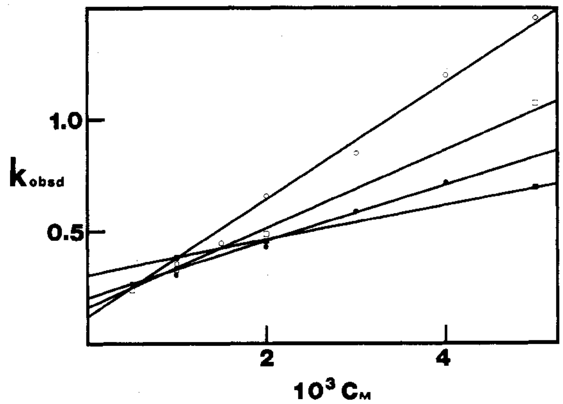

Figure 3. Plots of k_{obsd} (s^{-1}) against concentration of gallium perchlorate, C_M, for the reaction between gallium(III) and pyrocatechol violet at 25 °C and $I = 0.2$ M ($NaClO_4$): ○, $[H^+] = 0.05$ M; □, $[H^+] = 0.075$ M; ●, $[H^+] = 0.1$ M; ■, $[H^+] = 0.2$ M.

where k_f and k_d are formation and decomposition rate constants, respectively, and depend on pH. Their ratio must equal β_{11}. This is shown in Figure 2 where k_f/k_d, as obtained from slopes and intercepts of straight lines of Figure 3, are plotted against $1/[H^+]$ (squares).

For a better evaluation of kinetic parameters of the reverse reaction, the decomposition of the complex was also investigated. The complex was formed by mixing equal, small, amounts (2×10^{-5} M) of the reactants at pH >3, and the course of its decomposition, after mixing with $HClO_4$, was monitored. In these conditions the concentration of free gallium is negligibly small and eq 16 is reduced to $k_{obsd} = k_d$. A plot of k_d against $[H^+]$ gives a straight line with positive intercept and slope, meaning that paths zero and first order with respect to $[H^+]$, respectively, are operative in the reverse reaction (Figure 4).

These results are rationalized by the reaction scheme

$$Ga^{3+} + H_3L^- \rightleftharpoons GaH_2L^+ + H^+ \qquad (IA)$$

$$GaOH^{2+} + H_4L \rightleftharpoons GaH_2L^+ + H^+ \qquad (IB)$$

$$GaOH^{2+} + H_3L^- \rightleftharpoons GaH_2L^+ \qquad (IIA)$$

$$Ga(OH)_2^+ + H_4L \rightleftharpoons GaH_2L^+ \qquad (IIB)$$

Paths IA and IB are kinetically indistinguishable as well as paths IIA and IIB. Therefore only upper limits for their rate constants can be calculated. If the vertical protolytic equilibria of gallium(III) and PCV are fast in comparison with complexation reactions, the reaction scheme (IA)–(IIB) leads to an equation for k_{obsd} which can be written

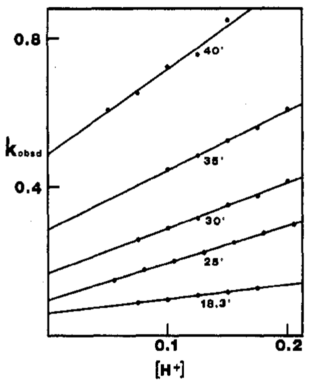

Figure 4. Plots at different temperatures of $k_{obsd} = k_d$ (s^{-1}) against $[H^+]$ for the decomposition of the gallium(III)–pyrocatechol violet complex at $I = 0.2$ M ($NaClO_4$).

Table II. Rate Constants[a] for Reaction Paths of the Gallium(III)–Pyrocatechol Violet Reaction at Different Temperatures and $I = 0.2$ M ($NaClO_4$)

T/°C	$k_I/M^{-1}\,s^{-1}$	k_{II}'/s^{-1}	$k_{-I}/M^{-1}\,s^{-1}$	$10k_{-II}/s^{-1}$
18.3	35 ± 7	5.17 ± 0.94	0.40 ± 0.04	0.59 ± 0.05
25[b]	65 ± 9	8.7 ± 0.4	1.01 ± 0.05	0.95 ± 0.06
25	88 ± 13	8.3 ± 1.3	1.01 ± 0.05	0.95 ± 0.06
30	107 ± 19	14.6 ± 2.4	1.23 ± 0.09	1.67 ± 0.12
35	140 ± 31	25.1 ± 5.0	1.59 ± 0.20	2.86 ± 0.29
40	201 ± 44	42.8 ± 6.4	2.30 ± 0.27	4.88 ± 0.27

[a] Due to proton ambiguity, k_I must be regarded as $k_{IA} + k_{IB}Q_{H1}/Q_A$ and k_{II}' must be regarded as $k_{IIA}Q_{H1} + k_{IIB}Q_{H1}Q_{H2}/Q_A$. [b] Data obtained with eq 17.

$$k_{obsd} = (k_I + k_{II}'/[H^+])C_M/\alpha\gamma + k_{-I}[H^+] + k_{-II} \qquad (17)$$

where $k_{II}' = k_{II}Q_{H1}$.

The rigorous least-squares adjustment given by Wentworth[7] was applied to 45 kinetic data points in order to obtain k_I and k_{II}'. Weights were given by setting an error of 10% in k_{obsd} and an error of 1% in concentrations. The values of k_{-I} and k_{-II}, known from results of Figure 4, were introduced as constant parameters. The values of k_I and k_{II}', which do minimize the squares of the weighed residuals, are quoted in Table II. An alternative treatment can be done by using the relationship $k_f/k_d = \beta_{11}$ and $k_I/k_{-I} = k_{II}'/k_{-II} = Q_{11}$. This leads to the rate equation

$$\frac{k_{obsd}}{(1 + \beta_{11}C_M)/Q_{11}} = k_{II}' + k_I[H^+] \qquad (18)$$

A plot of the left-hand side of eq 18 against $[H^+]$ is linear and yields $k_I = 76 \pm 6.5\ M^{-1}\,s^{-1}$ and $k_{II}' = 8.4 \pm 0.3\ M^{-1}\,s^{-1}$.[11]

From the known values of k_{-I} and k_{-II} at different temperatures and from the equation $k_I = k_{-I}Q_{11}$ (see Discussion), the temperature dependence of k_I has been obtained. Activation parameters calculated from data of Table II are $\Delta H^*(k_I) = 13 \pm 2$ kcal mol^{-1}, $\Delta S^*(k_I) = -7$ eu; $\Delta H^*(k_{-I}) = 13.1 \pm 1.1$ kcal mol^{-1}, $\Delta S^*(k_{-I}) = -15$ eu; $\Delta H^*(k_{-II}) = 17.3 \pm 1.1$ kcal mol^{-1}, $\Delta S^*(k_{-II}) = -5$ eu.

Discussion

Equilibria. Our value of Q_A at 25 °C in 1 M NaCl is somewhat higher than the literature datum[12] ($Q_A = 0.55$ M). We ascribe this difference to the different range of $[H^+]$ in which the measurements have been carried out. The authors of ref 12 have calculated Q_A from measurements at different wavelengths, but only data at pH 0.42 and 1.01 are suitable in order for a significant value to be obtained. Our value at

555 nm is calculated with 31 data points by changing [H^+] from 0.5 to 0.8 M. The value of Q_A at $I = 0.2$ M is affected by a larger error introduced by the need of working at concentrations of hydrogen less than 0.2 M where the species H_4L is present in low concentrations.

The value of Q_{11} decreases with increasing ionic strength as expected for eq 11.

From the acidity dependence of β_{11} and β_{21}, it is inferred that the attack of gallium(III) at H_3L^- ion involves formation of chelates and the protons present at the two reaction sites, which are in turn involved, are displaced. This is quite usual in complexation reactions of small highly charged ions,[5,13] although in the reaction of gallium(III) with 5-nitrosalicylate ions[14] the formation of a complex, $GaHL^{2+}$, in which the proton is retained, is noticed.

Kinetics. Reaction paths involving H_2L^{2-}, HL^{3-}, and L^{4-} have been ruled out because of the very low relative concentrations of these species in our solutions ($pK_{H_2L^{2-}} = 7.5$).[12] Reaction between Ga^{3+} and H_4L and reaction between $Ga(OH)_2^+$ and H_3L^- have not been included in the reaction scheme because the observed pH dependence provided no evidence for these reactions. The agreement of the ratios k_I/k_{-I} and k_{II}'/k_{-II} between themselves and with the spectrophotometric value of Q_{11} provides a good check of the validity of the kinetic pattern represented by reactions IA–IIB.

In the following discussion we shall assume that the experimental rate constants for complex-formation reactions equal the product $K_{os}k^*$, where K_{os} is the stability constant of an outer-sphere complex which is rapidly formed and k^* is the rate constant for the step of penetration of the ligand into the inner coordination shell of the metal ion. In order to assess a possible correlation between reactivity and basicity of the entering group, we have calculated[16] the values of k^* at 25 °C for reactions of Ga^{3+} with H_3L^-, sulfate, and salicylate ion ($HSAL^-$). They lie in the order $k^*_{H_3L^-}:k^*_{SO_4^{2-}}:k^*_{HSAL^-} = 16:13:130\ s^{-1}$. The more basic salicylate ion, $pK = 3$, is the more reactive whereas H_3L^- displays the same reactivity as SO_4^{2-} ion despite its lower basicity ($pK_{H_3L^-} = 0.39$, $pK_{SO_4^{2-}} = 2$). It is interesting to note however that all k^* values are at least 1 order of magnitude below the value of the rate constant for the process of water exchange ($k_{H_2O} = 1800\ s^{-1}$), and this has been taken as evidence for associative or concerted mechanisms.[15]

A second argument against the dissociative character of reaction IA is offered by the low values of the activation parameters. One can calculate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the process of conversion of the outer-sphere complex, $\{Ga(H_2O)_6,H_3L\}^{2+}$, into the corresponding inner-sphere complex, $\{Ga(H_2O)_5H_3L\}^{2+}$, by subtracting from $\Delta H^{\ddagger}(k_I)$ and from $\Delta S^{\ddagger}(k_I)$ the values of ΔH° and ΔS°, respectively, for the ion-pairing process.[13] With the Fuoss equation we calculated (for $a = 5$ Å and $Z_M Z_L = 3$) $\Delta H^\circ = 0.43$ kcal mol^{-1} and $\Delta S^\circ = 4.7$ eu. The activation parameters for conversion of the outer sphere to inner sphere are therefore $\Delta H^{\ddagger}(k^*) = 12.5$ kcal mol^{-1} and $\Delta S^{\ddagger}(k^*) = -12$ eu.

Activation parameter values for the water-exchange process[2] are $\Delta H^{\ddagger}(k_{H_2O}) = 6.3$ kcal mol^{-1} and $\Delta S^{\ddagger}(k_{H_2O}) = -22$ eu.

The values of k^* for reactions of $GaOH^{2+}$ with the above-mentioned ligands were also calculated[16] from the ratios k_{II}/K_{os} at 25 °C and are given in the sequence $k^*_{H_3L^-}:k^*_{SO_4^{2-}}:k^*_{HSAL^-} = 5000:1100:19000\ s^{-1}$. The enhanced reactivity of the hydrolyzed species is evident. In this case, too, a clear dependence on the ligand basicity is not assessed. It should be noted however that, due to proton ambiguity, the values of rate constants reported in both these sequences must be regarded as upper limits and that possibly both paths A and B are operative. Moreover, the nature of the ligands compared here is very heterogeneous and perhaps the basicity scale is not the most appropriate for our purpose in the sense that other factors such as polarizability and dimensions of the ions are probably important in determining not only the order of reactivities but also the reaction mechanism.

In conclusion, the features of the reactions of the hydrolyzed species remain obscure also because the rate constants for the water-exchange process of $GaOH^{2+}$ ion and related activation parameters are not available. The limited information in our possession does not enable us to exclude a dissociative mechanism for reactions of the kind (IIA). A dissociative mode of activation is not unreasonable if one considers that as the positive charge at the central atom decreases, the chance of a dissociative mechanism increases.[17] Moreover, the introduction of OH^- ion in the solvation shell of metal ion and the consequent labilization of the remaining water molecules[18] might result in an S_N1 process by decreasing the energy necessary to break the bond between metal ion and the water oxygen.

Registry No. Ga^{3+}, 22537-33-3; Ga, 7440-55-3; PCV, 115-41-3.

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(11) Although the two treatments lead to the same results, we have preferred the first one because all rate parameters have been obtained by making no use of the stability quotients. This enables us to take the agreement between equilibrium and kinetic experiments as a check of the validity of our model.

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(18) M. Eigen in "Advances in the Chemistry of Coordination Compounds", S. Kirschner, Ed., Macmillan, New York, 1961, p 371.