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Mechanism of the Complex Formation between Aluminum and Sulfosalicylate Ions. Role of the Hydrolyzed Metal Ion

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The kinetics of the reaction between Al(III) and the ions of 5-sulfosalicylic acid, H_3L, were investigated in the pH range between 1.3 and 4.1 at 25 °C and at an ionic strength of 0.1 M. The results were interpreted in terms of three reaction paths; some evidence for an additional path, namely, that between Al^{3+} and H_2L^-, was also obtained, and an upper limit of 0.02 M^{-1} s^{-1} was estimated for the rate constant. The pathway via $AlOH^{2+}$ and HL^{2-} has the much higher rate constant of 2.5×10^3 M^{-1} s^{-1}, confirming the enhanced reactivity of the hydrolyzed cation. Two other pathways, involving $AlOH^{2+}$ + H_2L^- and Al^{3+} + HL^{2-}, respectively, have exactly the same pH dependence. If the rate constant of the former path is assumed to be calculable from the rate of similar reactions, then that of the latter becomes ~ 1.5 M^{-1} s^{-1}, higher than normal for the charge type in question but not significantly so. This result is discussed in terms of "internal hydrolysis". No retarding influence of the internal hydrogen bond was observed, nor was there any sign of rate-determining ring closure. The results were obtained by the stopped-flow technique or by following the reaction spectrophotometrically with the aid of a recorder.

Introduction

The mechanism of the formation of labile complexes is by now well established. According to the Eigen mechanism[1] the observed rate constant equals $K_{os}k^*$, where K_{os} is an outer-sphere association constant and k^* the first-order constant for the rate at which the ligand present in the outer sphere changes places with a water molecule in the inner coordination sphere of the metal ion.

For some labile metal ions which undergo strong hydrolysis the mechanism is complicated by the labilizing effect of OH^- on the remaining water molecules in the inner coordination sphere[2] and by the possibility of "internal hydrolysis" when the metal reacts with the anion of a weak acid.[2] Whereas these problems have been investigated and discussed in detail for Fe(III),[3] comparatively few data[4-9] are available for Al(III) which has the drawback of forming much weaker complexes and of exhibiting no absorbance in an accessible wavelength range.

Additional data on systems involving Al(III) seemed desirable in order to get some insight into the role of the hydrolyzed species.

Using pH indicators to monitor the reaction, we have not been able to detect the formation, to a significant extent, of a complex between Al(III) and acetic acid, in a range of pH and concentration where the complications arising from polymerization and further hydrolysis can be neglected.

For the present investigation, we therefore chose the chelating ligand 5-sulfosalicyclic acid which we shall abbreviate as H_3L. The reaction can be monitored spectrophotometrically, owing to the difference in absorbance between the complex and the free ligand. The ion H_2L^- is the anion of a strong acid, and the ion HL^{2-} that of a moderately strong acid ($pK = 2.4$).

Experimental Section

Materials. An acidified stock solution of $Al(ClO_4)_3 \cdot 8H_2O$ was prepared from Fluka "purum" salt and perchloric acid (Merck). The metal ion concentration was determined by direct titration with EDTA in the presence of Cu^{2+} using PAN as an indicator.[10]

Stock solutions of the 5-sulfosalicylic and perchloric acids were prepared and were titrated with CO_2-free sodium hydroxide solution.

The ionic strength was 0.1 M, regulated by the addition of sodium perchlorate (Fluka puriss.).

Instruments. The pH of the solutions was measured with a digital pH meter (Radiometer PHM52) having an accuracy of ±0.005 unit of pH. All spectrophotometric measurements were carried out with a Hilger-Gilford spectrophotometer.

Kinetic measurements in the higher pH range were carried out by the stopped-flow technique, using an Aminco-Morrow apparatus. Oscilloscope traces were analyzed by transferring the data to punched cards by means of a magnifying manual trace-follower coupled to an analog to digital converter and processing the cards in a CDC computer.

In the lower pH range the reactions were so slow that they could be followed with the aid of our spectrophotometer. Its output measures directly the optical density and was recorded on a Honeywell recorder.

At pH ≥ 2.0 formation rates were measured by mixing suitable solutions of Al(III) and ligand. At lower pH the degree of complexation is very low; therefore, decomposition rates were measured by mixing the complex with perchloric acid solution. At pH 2.0 both methods were employed and yielded identical results.

The concentration of aluminum, a, was varied between 1.0×10^{-3} and 5.8×10^{-3} M and was always much higher than that of the ligand, b, which was 10^{-4} to 2×10^{-4} M. The formation of complexes in which the ratio of ligand to metal ion is higher than unity can therefore be

Table I. Apparent Stability Constants of Aluminum Monosulfosalicylate at $I = 0.1$ M and $T = 25$ °C

$10^3[H^+]$, M	K_{app}	$10[H^+]/[K_{app}([H^+] + K_{OH})]^a$	λ, nm
10.615	1.93	5.177	315
4.197	3.77	2.651	315
4.197	3.57	2.797	310
1.762	5.03	1.986	315
1.762	5.15	1.933	310

^{a} Nonsignificant figures are retained in order to enable a statistical analysis to be carried out.

neglected. The pH was varied between 1.3 and 4.1 and was regulated by the addition of small amounts of perchloric acid or sodium hydroxide solutions. The concentration of H^+ was taken as antilog $(-pH)/\gamma_\pm$, with $\gamma_\pm = 0.78$, calculated from the Davies equation.[11]

The temperature was 25 °C throughout.

Results

Equilibrium Constants. The formation constant of our complex from Al^3+ and HL^2- is

$$K_1 = [AlL][H^+]/[Al^{3+}][HL^{2-}] \qquad (I)$$

However, the quantity amenable to measurement by spectrophotometric methods is an "apparent" equilibrium constant K_{app}, the formation constant of the complex from the total uncomplexed participants. From the data of Frink and Peech[12] we calculate that, in our range of concentrations, the presence of metal species other than Al^3+ and AlOH^2+ (such as dimers, polymers, or more highly hydrolyzed species) can be neglected up to pH ~3.5. Furthermore, both H_3L and L^3- ($pK^{13} = 11.5$–12) are present at negligible concentrations. Therefore

$$K_{app} = \frac{[AlL][H^+]}{([Al^{3+}] + [AlOH^{2+}])([HL^{2-}] + [H_2L^-])} = \frac{K_1 K_H [H^+]}{(K_{OH} + [H^+])(K_H + [H^+])} \qquad (II)$$

where K_{OH} is the hydrolysis constant of aluminum, and K_H the dissociation constant of the carboxylic group.

In the wavelength range between 310 and 315 nm the absorbance of the complex is much stronger than that of the free ligand. After a suitable transformation of the expression for the absorbance A measured in solutions containing aluminum ion at concentration a and ligand at total concentration b, with $a \gg b$, we get

$$\frac{b}{A - b\epsilon_L} = \frac{1}{\epsilon_{AlL} - \epsilon_L} + \frac{[H^+]}{(\epsilon_{AlL} - \epsilon_L)K_{app}a} \qquad (III)$$

where ϵ_{AlL} and ϵ_L are the absorption coefficients of ligand and complex at the measured pH.

At constant pH a plot of the left-hand side of eq III against $1/a$ is a straight line from whose slope and intercept we get K_{app}. The results are summarized in Table I. The measurements were carried out between pH 2 and 3. At higher values of pH the degree of complexation was too high and at lower values of pH it was too low for satisfactory results to be obtained.

The relationship between K_1 and K_{app} can be written in the form

$$\frac{[H^+]}{K_{app}([H^+] + K_{OH})} = \frac{1}{K_1} + \frac{[H^+]}{K_1 K_H} \qquad (IV)$$

The hydrolysis constant at our ionic strength, calculated from the thermodynamic constant given by Frink and Peech,[12] using the Davies equation,[11] is $K_{OH} = 3.55 \times 10^{-6}$ M.

By plotting the left-hand side of eq IV against [H^+] we get a straight line (see Figure 1) which yields $K_1 = 7.6 \pm 0.5$ and

Table II. Kinetic Data for the Aluminum–Sulfosalicylic Acid System at $I = 25$ °C

10^3a, M	pH	10^2k_{obsd}, s^-1	$10^2k_{f'}$,^{a} s^-1	$[H^+]^{-1}$,^{a} M^-1
4.83	4.090	500	411.8	9596.1
5.17	3.920	139	106.9	6487.8
4.83	3.760	34.0	28.28	4488.4
4.83	3.550	11.6	9.874	2767.5
4.83	3.450	9.70	8.402	2198.3
4.83	3.310	6.70	5.993	1592.6
5.79	3.060	4.46	3.640	895.56
5.79	3.055	4.49	3.673	885.31
4.14	3.050	3.13	3.545	875.18
2.07	3.050	1.54	3.372	875.18
4.83	3.040	3.40	3.337	855.25
4.83	3.020	3.48	3.445	816.76
4.83	2.940	2.80	2.876	679.35
4.83	2.750	1.74	1.980	438.63
4.83	2.590	1.14	1.426	303.46
5.17	2.420	1.045	1.357	205.16
4.83	2.160	0.73	1.053	112.74
2.59	2.140	0.65	1.201	107.67
7.76	2.095	1.01	1.106	97.07
5.17	2.050	0.71	0.958	87.52
1.03	2.040	0.51	1.069	85.53
5.17	2.020	0.89	1.182	81.69
5.17	2.000	0.88	1.157	78.00
5.17	1.710	0.95	0.8988	40.00
5.17	1.560	1.28	0.9334	28.32
5.17	1.440	1.59	0.9159	21.48
5.17	1.330	1.90	0.8695	16.68

^{a} Nonsignificant figures are retained in order to enable a statistical analysis to be carried out.
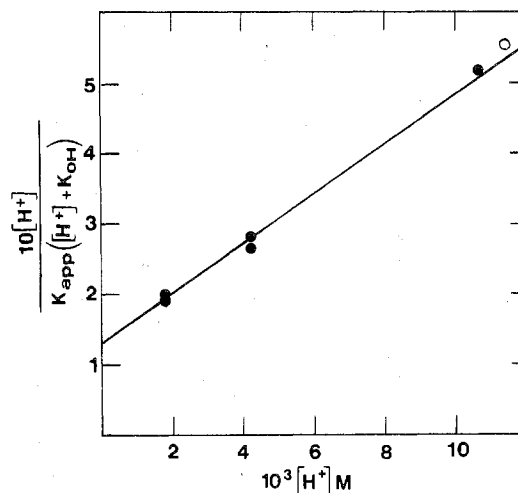

Figure 1. Dependence of $[H^+]/K_{app}([H^+] + K_{OH})$ on $[H^+]$ (see eq IV); the circle is the kinetic result.

$K_H = (3.75 \pm 0.13) \times 10^{-3}$ M from the intercept and from the ratio of intercept and slope, respectively. The fact that the plot corresponding to eq IV is indeed a straight line confirms the assumption implicit in eq II, namely, that the only complex formed under our conditions is the fully deprotonated AlL.

Kinetics of Reaction. Since a and [H^+] were always high in comparison with b, our reaction follows pseudo-first-order kinetics, with an observed rate constant

$$k_{obsd} \equiv d \ln ([AlL] - [AlL]_\infty)/dt \qquad (V)$$

The results are shown in Table II. At constant pH, k_{obsd} must be a linear function of a, which we shall find convenient to write

$$k_{obsd} = k_f a + k_d [H^+] \qquad (VI)$$

where k_f and k_d are the formation and dissociation rate
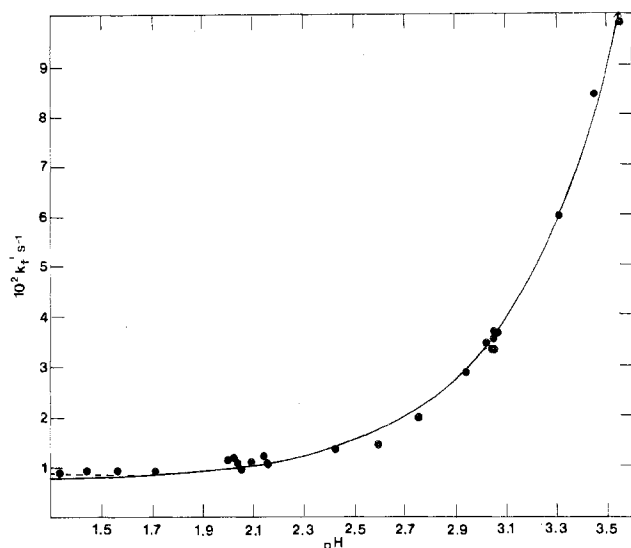
Figure 2. pH dependence of $k_f' = k_{obsd}K_HK_1/K_{app}B = k_1K_H + k_2K_{OH} + k_3[H^+] + k_4K_HK_{OH}/[H^+]$: full curve, synthesized on the basis of reactions 1, 2, and 4; broken line, synthesized on the basis of reactions 1-4.

constants, respectively, and depend on pH. Furthermore,[14] $k_f/k_d = K_{app}$. The linearity was confirmed at pH $\sim$3 and around 2.05. In the former case, k_d was too small for K_{app} to be calculated; in the latter case, we got K_{app}=1.8. This is inserted as a circle in Figure 1 and is seen to be in satisfactory agreement with the spectrophotometric results.

Possible reactions are

$$Al^{3+} + HL^{2-} \rightleftharpoons AlL + H^+ \tag{1}$$

$$AlOH^{2+} + H_2L^- \rightleftharpoons AlL + H^+ + H_2O \tag{2}$$

$$Al^{3+} + H_2L^- \rightleftharpoons AlL + 2H^+ \tag{3}$$

$$AlOH^{2+} + HL^{2-} \rightleftharpoons AlL + H_2O \tag{4}$$
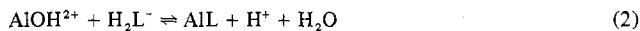
where the vertical equilibria are all rapid in comparison with the rate of complex formation.[15] In analogy with relaxation experiments the reaction scheme (1)–(4) leads to an expression for k_{obsd} which can be written

$$k_{obsd} = (k_1K_H + k_2K_{OH} + k_3[H^+] +$$

$$k_4K_HK_{OH}/[H^+])(K_{app}/K_1K_H)B \tag{VII}$$

with

$$B = a + [H^+]/K_{app} \tag{VIII}$$

Comparing these expressions with eq VI we can easily derive that $k_{obsd}/B = k_f$. The quantity in the first parentheses on the right-hand side of eq VII is $k_fK_1K_H/K_{app}$ and will be abbreviated as k_f'. The dependence of this quantity on pH is given in Figure 2. Figure 3 shows a plot of k_f' as a function of $[H^+]^{-1}$, up to pH 3.55. A straight line is seen to be obtained, with no noticeable upward trend at low values of $[H^+]^{-1}$. This shows the contribution of the term $k_3[H^+]$ to be very small. Nevertheless, in calculating the slope and intercept of our line we did not include the points at pH $\leq$1.56 (see below). The results are

intercept $= k_1K_H + k_2K_{OH} = (7.0 \pm 0.5) \times 10^{-3} \text{ s}^{-1}$

and

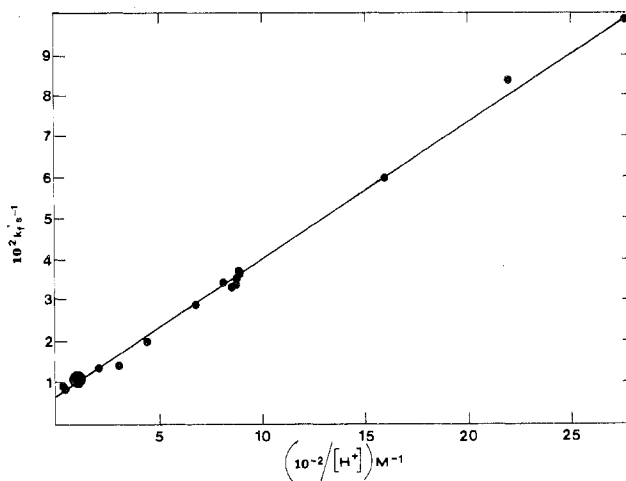slope $= k_4K_HK_{OH} = (3.33 \pm 0.05) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$

Figure 3. Values of k_f' as a function of $1/[H^+]$. The large dot comprises 7 experimental points.

If reaction 3 were entirely negligible, then k_f' should continue to decrease with increasing $[H^+]$. The fact that this is not the case (see Figure 2) hints at some contribution by this path. On the assumption that k_f' goes through a just discernible minimum at pH $\sim$1.5 we can estimate

$$k_3 \leqslant k_4K_HK_{OH}/[H^+]^2_{min} = 0.02 \text{ M}^{-1} \text{ s}^{-1}$$

At pH above 3.55 the values of k_f' increased much more steeply with increasing $1/[H^+]$ than would correspond to the straight line in Figure 3. The effect must be ascribed to additional paths with a rate proportional to $1/[H^+]$ to powers higher than unity. They may involve more highly hydrolyzed species of Al(III). In view of the complexity of these systems[17] we did not attempt a quantitative evaluation of these measurements. Similar effects were observed in the reaction with salicyclic acid.[7]

Discussion

Equilibrium Constants. For K_H at our ionic strength the values reported in the literature[13] vary between 8×10^{-3} and 2.5×10^{-3} M. Our value of 3.75×10^{-3} M lies within these limits.

Similarly, our result for K_1 lies within the limits of the various results reported[13,18] when the range of values given for the two dissociation constants of sulfosalicylic acid is taken into account.

Rate Constants. We calculated the outer-sphere association constants from the Fuoss equation,[19] taking 5 Å as the distance of approach of the ions and correcting for the ionic strength with the aid of the Davies equation.[11] The result depends on the charge type. Since charges far removed from the reaction site have been found to have little influence on the reaction rate,[20-22] we ignore the negative charge on the SO_3^- group.

We assume k^*, the rate constant for the exchange between ligand and water in the inner coordination sphere, to be equal to k_{H_2O}, the rate constant for water exchange between bulk and inner sphere, times a statistical factor[23] of 0.75. For k_{H_2O} on Al^{3+} Fiat and Connick[24] estimated a value of 0.13–0.22 s^{-1} from an ^{17}O magnetic resonance study. This leads to $k^* \approx 0.13$ s^{-1}, in reasonable agreement with 0.085 s^{-1} given for[6] $Co(CN)_6^{3-}$ (though considerably lower than the values for[4] $Fe(CN)_6^{3-}$ and[5] SO_4^{2-}).

On this basis we should expect k_3 to be $\sim$0.04 M^{-1} s^{-1}, to be compared with our value of $k_3 \leq 0.02$ M^{-1} s^{-1}. The estimate is too uncertain for us to decide whether or not the reduction of the rate is significant, as it is for cations forming more labile complexes with ligands containing an internal hydrogen bond.[22] (Our experiments were not carried down to lower values of pH where this question might be decided, because in the

present investigation we are primarily interested in paths involving AlOH^{2+}; lower values of pH would have necessitated a higher ionic strength and would have entailed the additional complication that the concentration of H$_3$L could no longer be neglected.)

We next consider reaction 4. From the slope of Figure 3 we calculate, again using $K_{OH} = 3.55 \times 10^{-6}$ M, that

$$k_4 = (2.50 \pm 0.04) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

and

$$k^* = 1.22 \times 10^3 \text{ s}^{-1}$$

Comparison with the value of ~ 0.13 s^{-1} for Al^{3+} confirms the labilizing effect of OH$^-$ on the remaining water molecules in the inner coordination sphere.

No direct measurements of the rate of water exchange on AlOH^{2+} seem to be available. For the reaction with the monoprotonated anion of salicylic acid (a system very similar to the present one) Secco and Venturini[7] found a rate constant which is lower than ours by a factor of ~ 2.5. These authors, however, used[25] $K_{OH} = 8.3 \times 10^{-6}$ M, whereas we prefer a more recent value.[12] When this is taken into account, their result becomes almost exactly equal to ours.[26]

We now turn our attention to the intercept of Figure 3. This is composed of the contributions of two reactions, (1) and (2), which exhibit "proton ambiguity", that is to say, have exactly the same pH dependence. If the whole intercept were equal to k_1K_H, we should get

$$k_1 = 1.87 \text{ M}^{-1} \text{ s}^{-1}$$

higher by a factor of almost 3 than the value of ~ 0.7 M^{-1} s^{-1} calculated from the rate of water exchange.

On the other hand, if the whole intercept were equal to k_2K_{OH}, we should get

$$k_2 = 2.00 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

and for the ligand–water exchange on AlOH^{2+} we should get $k^* \approx 6.3 \times 10^3$ s^{-1}, about 5 times higher than the value obtained from our reaction 4.

In the light of these results we conclude that both reactions contribute to the [H$^+$]-independent term in eq VII. In order to proceed further, we have to assume k^* to be known for one of the two reactions. It seems reasonable to assume that k^* for reaction 2 should be similar to that for reaction 4 (and for the analogous reaction[7] for salicylic acid). On this basis the contribution of reaction 2 to our intercept would be only $\sim 10^{-3}$ s^{-1}. This leaves $\sim 6 \times 10^{-3}$ s^{-1} for the contribution of reaction 1 which leads to

$$k_1 \approx 1.5 \text{ M}^{-1} \text{ s}^{-1}$$

This value is certainly not abnormally *low*. This shows again[28] that the internal hydrogen bond on the ligand does not influence the kinetics the way it does in the case of more labile complexes.[22] Nor can the rate be influenced by the possible slowness of ring closure.[20]

Not only is our value not abnormally low, but it is still by a factor of 2 *higher* than that calculated from the rate of

water–ligand exchange. In view of the uncertainty of the assumptions made in order to arrive at this result and, further, in view of the discrepancies between the few values available in the literature[27] for systems involving Al(III), it is difficult to decide whether the factor is significant. Nevertheless, the fact that our rate constant is high gives some support to the idea of internal hydrolysis,[2] an idea originally brought forward in order to explain why ligands which are the anions of weak acids should react with Fe(III) at abnormally high rates. This explanation became redundant when the high reactivity of FeOH^{2+} was recognized,[29] but it might still remain valid if the rate constant for the unhydrolyzed form is found to be abnormally high *after* the contribution of the hydrolyzed form has been taken into account. This effect was noted by us[3] for Fe(III). It can make itself felt only when the ligand is the anion of a moderately weak (not very weak) acid where both paths make comparable contributions,[3] as they do in the present system.

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