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Mechanism of Ligand Substitution in Aluminum(III) Complexes

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Rate constant and activation parameter values have been determined for the ligand substitution reactions of $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5OH^{2+}$ with F^-. By monitoring the reactions with a fluoride ion selective electrode, we were able to determine overall rate constant values for these two reactions, and the Fuoss equation was then used to calculate values for ligand substitution rate constants. For fluoride ion ligand substitution in $Al(H_2O)_6^{3+}$, $k_s = 1.55 \pm 0.35$ s^{-1} at 25 °C, $\Delta H^* = 96.3 \pm 6.2$ kJ mol^{-1}, and $\Delta S^* = +82.9 \pm 21.2$ J mol^{-1} K^{-1}. For the same reaction with $Al(H_2O)_5OH^{2+}$, $k_s = 2196 \pm 282$ s^{-1} at 25 °C, $\Delta H^* = 83.7 \pm 5.0$ kJ mol^{-1}, and $\Delta S^* = +99.8 \pm 17.5$ J mol^{-1} K^{-1}. These findings are discussed along with supporting data that lead to the assignment of an I_a mechanism for fluoride ion substitution in $Al(H_2O)_6^{3+}$ and an I_d mechanism for fluoride ion substitution in $Al(H_2O)_5OH^{2+}$.

Introduction

There has been considerable recent interest in the mechanisms for water exchange of octahedral hexaaqua metal ions,[1,2] including aluminum.[3] However, for aluminum and other readily hydrolyzed metal ions, the mechanism of ligand substitution for ligands other than water is still uncertain.[4] The objective of this study was to determine the mechanisms of ligand substitution in the reactions of $Al(H_2O)_6^{3+}$ and $Al(H_2O)_5OH^{2+}$ with F^- in aqueous solution. F^- was the ligand of choice because we had done earlier environmental studies of aluminum fluoride kinetics[5,6] and because monitoring F^- by using an ion-selective electrode allows one to avoid the so called "proton ambiguity" that has caused uncertainties in earlier aluminum complexation kinetic results (see discussion below).

Experimental Section

Materials. All materials were prepared as described earlier.[5,6] Initial total aluminum concentrations were 5.00×10^{-5} M and were always in large excess over initial F^- concentrations to ensure that only the 1:1 aluminum–fluoride complex formed. The aluminum concentration was not varied because the reaction was known to be first order in aluminum at all pH values examined in this study.[5] Initial F^- concentrations ranged from 9.87×10^{-6} to 1.92×10^{-5} M.

In all solutions the pH was adjusted to the desired value with HCl, and the ionic strength was adjusted to 0.1 M by using NaCl. It has been shown that chloride ion does not complex aluminum.[7,8] Reactions were studied at several different pHs ranging from 2.88 to 4.06.

Kinetic Procedure. An Orion single-crystal lanthanum fluoride membrane electrode was immersed in the reaction mixture to be monitored along with a saturated calomel reference electrode. An Orion Model 701A digital pH meter was used to measure potential. In each run 101 mL of a F^- solution was thermostated at the desired temperature in a plastic beaker and stirred with a magnetic stirring bar coated with Teflon. A 1-mL sample of aluminum solution was then injected with an automatic pipet, and the potential was measured as a function of time. The response time of the fluoride ion selective electrode has been shown to be much less than 1 s and is capable of monitoring reactions that are faster than the aluminum–fluoride complexation reaction.[9]

Solution pH was determined by using a Markson 785 combination pH electrode connected to a Model 701A Orion digital pH meter. Standard buffers were used for reference with no corrections made for liquid-junction potential differences. The concentration of H^+ was taken as $[H^+] = 10^{-pH}/\gamma_{H^+}$, with $\gamma_{H^+} = 0.78$, calculated from the Davies equation,[10] where the square brackets denote concentration in moles per liter. The concentrations of all species were determined as molarities rather than activities. However, since the ionic strength was constant throughout, the molarity of each species differed from its activity by only a proportionality constant.

Table I. Initial Rates of Consumption of Fluoride Ion

$[H^+]$, M	pH	$[F^-]_0$, M × 10^5	init rate, M s^{-1} × 10^8	init rate/ $[Al^{3+}]_0[F^-]_0$, M^{-1} s^{-1}
		Temp = 27.5 °C		
1.73×10^{-3}	2.87	1.68	0.872 ± 0.026	10.4 ± 0.3
6.21×10^{-4}	3.31	1.63	1.84 ± 0.092	22.7 ± 1.1
5.01×10^{-4}	3.41	1.60	1.96 ± 0.196	24.7 ± 2.5
4.11×10^{-4}	3.49	1.51	2.26 ± 0.271	30.2 ± 3.6
		Temp = 25 °C		
1.68×10^{-3}	2.88	0.987	0.329 ± 0.010	6.68 ± 0.20
6.04×10^{-4}	3.33	1.57	1.07 ± 0.043	13.7 ± 0.55
4.99×10^{-4}	3.41	1.64	1.44 ± 0.115	17.7 ± 1.4
3.73×10^{-4}	3.54	1.48	1.56 ± 0.156	21.3 ± 2.1
		Temp = 22.5 °C		
1.65×10^{-3}	2.44	1.74	0.440 ± 0.013	5.07 ± 0.15
5.81×10^{-4}	3.34	1.57	0.824 ± 0.033	10.6 ± 0.42
4.96×10^{-4}	3.41	1.67	0.883 ± 0.071	10.7 ± 0.86
3.66×10^{-4}	3.54	1.44	1.08 ± 0.11	15.2 ± 1.5
		Temp = 20 °C		
1.63×10^{-3}	2.90	1.83	0.272 ± 0.005	2.98 ± 0.06
5.86×10^{-4}	3.34	1.65	0.496 ± 0.020	6.05 ± 0.24
4.97×10^{-4}	3.41	1.72	0.617 ± 0.037	7.23 ± 0.43
4.97×10^{-4}	3.41	1.70	0.608 ± 0.036	7.21 ± 0.43
		Temp = 7.5 °C		
1.86×10^{-3}	2.84	1.92	0.0393 ± 0.0008	0.409 ± 0.008
8.90×10^{-4}	3.16	1.86	0.0495 ± 0.0015	0.533 ± 0.016
6.24×10^{-4}	3.31	1.78	0.0607 ± 0.0024	0.683 ± 0.027
4.28×10^{-4}	3.48	1.73	0.0732 ± 0.0044	0.848 ± 0.051

Results and Discussion

Treatment of Data. Initial rates of free F^- consumption were determined by plotting $[F^-]$ vs time and drawing tangents to the curves at time $t = 0$. The slopes of the tangents then gave the initial rates of free F^- consumption, $(-d[F^-]/dt)_{t=0}$. Both plotting and slope determination were done with an Apple IIe computer using a commercial program called CURVE FITTER. The program produced least-squares fitting of data points to exponential equations from which initial rates were obtained directly. Table I gives the initial rate values so obtained, along with initial concentrations of fluoride and hydrogen ions. Initial rate values varied from about ±12% at pH 3.54 and 27.5 °C to approximately ±2% at pH 2.84 and 7.5 °C.

Rate Equation. Since we knew from previous experience that at sufficiently low pH the rate equation can be cast in a form in

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Table II. Observed Rate Constants, Calculated K_{os} Values, and Ligand Substitution Rate Constants

T, K	k_1, M^{-1} s^{-1}	$K_{os}{}^1$, M^{-1}	k_{s1}, s^{-1}	k_3, M^{-1} s^{-1}	$K_{os}{}^3$, M^{-1}	k_{s3}, s^{-1}
280.5	0.270 ± 0.026	1.70	0.158 ± 0.014	235 ± 30	0.968	243 ± 31
293	1.12 ± 0.10	1.60	0.700 ± 0.062	1183 ± 95	0.932	1269 ± 102
295.5	2.12 ± 0.43	1.59	1.33 ± 0.27	1555 ± 211	0.925	1681 ± 228
298	2.43 ± 0.55	1.57	1.55 ± 0.35	2018 ± 259	0.919	2196 ± 282
300.5	4.63 ± 1.01	1.55	2.99 ± 0.65	2493 ± 420	0.913	2731 ± 460

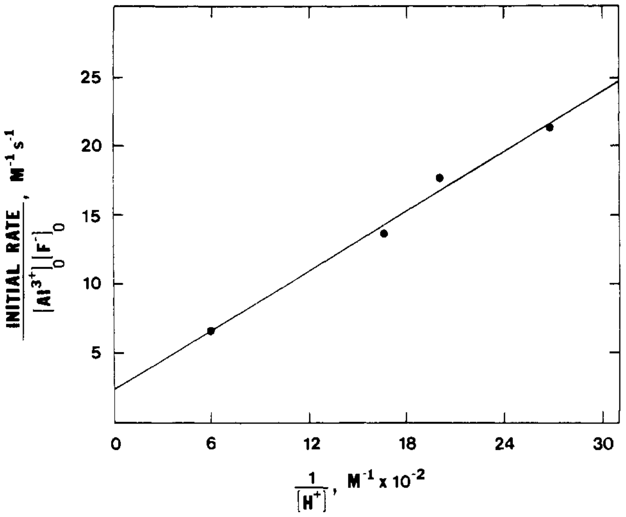

Figure 1. Initial rate/$[Al^{3+}]_0[F^-]_0$ vs $1/[H^+]$ at 25 °C.

which each term contains $[Al^{3+}][F^-]$,[6] we calculated initial rate/$[Al^{3+}]_0[F^-]_0$ values for each run, and these are shown in Table I as well. The initial rate/$[Al^{3+}]_0[F^-]_0$ values increased with increase in pH, and a plot of initial rate/$[Al^{3+}]_0[F^-]_0$ vs $1/[H^+]$ was linear up to a pH of about 3.54 ($[H^+] = 3.73 \times 10^{-4}$ M), as shown in Figure 1. This indicated a rate equation of the form

$$(-d[F^-]/dt)_{t=0} = k_I[Al^{3+}]_0[F^-]_0 + k_{II}[Al^{3+}]_0[F^-]_0/[H^+] \quad (1)$$

The following discussion of the mechanism is confined to pH values below about 3.54, where the only aluminum species initially present at significant concentrations were $Al(H_2O)_6{}^{3+}$ and $Al(H_2O)_5OH^{2+}$.[6,10,11]

Overall Mechanism. A possible mechanism for the reaction of aluminum with F^- at pH below 3.54 is as follows:

$$Al^{3+} + F^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AlF^{2+} \quad (2)$$

$$AlOH^{2+} + F^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} AlFOH^+ \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} AlF^{2+} \quad (3)$$

$$Al^{3+} + HF \underset{k_6}{\overset{k_5}{\rightleftharpoons}} AlF^{2+} + H^+ \quad (4)$$

$$AlOH^{2+} + HF \underset{k_8}{\overset{k_7}{\rightleftharpoons}} AlF^{2+} + H_2O \quad (5)$$

Coordinated waters have been omitted for simplicity. In addition, the following protolytic equilibrium must be considered:

$$Al^{3+} \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} AlOH^{2+} + H^+ \quad (6)$$

Using the initial rate method, one can neglect back-reactions in formulating the rate expression,[12] so the initial rate of consumption of F^- is given by

$$(-d[F^-]/dt)_{t=0} = k_1[Al^{3+}]_0[F^-]_0 + k_3[AlOH^{2+}]_0[F^-]_0 \quad (7)$$

Assuming that the protolytic reaction 6 is rapid in comparison to complexation[9,10] yields

$$[AlOH^{2+}]_0 = k_{11}[Al^{3+}]_0/k_{12}[H^+] \quad (8)$$

Substitution of eq 8 into eq 7 gives

$$(-d[F^-]/dt)_{t=0} = k_1[Al^{3+}]_0[F^-]_0 + k_3k_{11}[Al^{3+}]_0[F^-]_0/k_{12}[H^+] \quad (9)$$

which is identical to the experimental rate equation, eq 1.

At this point it is important to note that the rate of consumption of F^- is not the same as the rate of appearance of AlF^{2+}. That can be seen by considering eq 10.[9]

$$[F^-] = [F]_{total} - [HF] - [AlF^{2+}] \quad (10)$$

Equation 10 yields

$$-d[F^-]/dt = d[AlF^{2+}]/dt + d[HF]/dt \quad (11)$$

Thus, any method that monitors the rate of appearance of product in aluminum complexation reactions differs from the present method of monitoring the rate of consumption of F^-. By the monitoring of the rate of F^- consumption, the so-called "proton ambiguity"[4,10] has been eliminated, and the intercept of Figure 1 is equal to k_1. k_3 can be obtained from the slope of Figure 1.

Rate Constants. The general mechanism of Eigen[13] for ligand substitution reactions of octahedral complexes is shown in reaction 12. In this scheme $k_f/k_r = K_{os}$, and if $K_{os}[L] \ll 1$, then observed

$$(H_2O)_6M^{n+} + L^{m-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (H_2O)_6M,L^{+n-m} \xrightarrow{k_s} (H_2O)_5ML^{+n-m} + H_2O \quad (12)$$

second-order rate constants consist of the product of K_{os} and a ligand substitution rate constant, k_s, so that $k_1 = K_{os}{}^1k_{s1}$ and $k_3 = K_{os}{}^3k_{s3}$.[14] K_{os} values can be estimated by use of the Fuoss equation.[15] A problem is calculating K_{os} values is in choosing the proper distance of separation of the two ions in the outer-sphere complex.[16] In past aluminum kinetics studies a value of 5.0 Å, representing a single hydration layer, has been used.[10,11] However, if the ligand is strongly solvated, the metal ion and ligand may be separated by two hydration layers.[16] Since F^- can be expected to be strongly solvated in aqueous solution,[17] the aluminum and fluoride ions in the outer-sphere complex may be separated by two hydration layers, or about 7.5 Å.[16] Table II shows the values of the observed rate constants for reactions 2 and 3, calculated K_{os} values for a two hydration layer separation, and the resulting ligand substitution rate constants at five different temperatures. Errors in k_1 and k_3 were estimated graphically from errors in initial rate/$[Al^{3+}]_0[F^-]_0$ values.[18]

Activation parameter values were obtained from the variation of k_{s1} and k_{s3} with temperature.[19] For reaction 13, $\Delta S^* = +82.9$

$$(H_2O)_6Al,F^{2+} \xrightarrow{k_{s1}} (H_2O)_5AlF^{2+} + H_2O \quad (13)$$

$\pm$ 21.7 J mol^{-1} K^{-1} and $\Delta H^* = 96.3 \pm 6.2$ kJ mol^{-1}. For reaction 14, $\Delta S^* = +99.8 \pm 17.5$ J mol^{-1} K^{-1} and $\Delta H^* = 83.7 \pm 5.0$ kJ mol^{-1}.

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$$(H_2O)_5AlOH,F^+ \xrightarrow{k_{s3}} (H_2O)_4AlOHF^+ + H_2O \qquad (14)$$

Mechanism of Ligand Substitution. It has long been recognized that $Al(H_2O)_5OH^{2+}$ is considerably more labile than $Al(H_2O)_6^{3+}$ in ligand substitution reactions.[4,10] The smaller value of ΔH^* and larger value of ΔS^* of reaction 14 as compared to the same values for reaction 13 are therefore as expected. (In fact, using ΔH^* and ΔS^* values to calculate the ratio k_{s3}/k_{s1} gave 1640 at 280.5 K as compared to the determined value of 1540.) The rather large positive value of ΔS^* for reaction 14 can be accounted for by an I_d mechanism[20] of ligand substitution in $Al(H_2O)_5OH,F^+$. Indeed, the bulk of information in the literature indicates that aluminum complexes in aqueous solution undergo ligand substitution by I_d mechanisms.[11,15,21,22]

Hugi-Cleary et al.[3] have proposed an I_d mechanism for the exchange reaction of $Al(H_2O)_6^{3+}$ with solvent H_2O on the basis of ΔV^* and ΔS^* values of $+5.7 \pm 0.2$ cm^3 mol^{-1} and $+41.6 \pm 0.9$ J mol^{-1} K^{-1}, respectively. They obtained a value for k_{ex} of 1.29 ± 0.04 s^{-1} at 25 °C. k_{ex} in $Al(H_2O)_6^{3+}$ is much smaller than the value of 2196 ± 282 s^{-1} for k_{s3} in $Al(H_2O)_5OH,F^+$, due partially to the labilizing effect of hydroxide.[4,10,14,23] Unfortunately, k_{ex} has not been determined for $Al(H_2O)_5OH^{2+}$, and so direct comparison with k_{s3} is not possible.

We can, however, compare k_{s1} with k_{ex} in $Al(H_2O)_6^{3+}$. In order to do so, a statistical correction must be applied because of the difference in the solvation shells of the activated complexes. k_{s1} will be increased relative to k_{ex} by a statistical correction factor S, such that $k_1 = SK_{os}k_{s1}$.[22] Assuming $S = {}^3/_4$[22,24,25] yielded a value of 2.06 ± 0.47 s^{-1} for k_{s1}, while $k_{ex} = 1.29 \pm 0.04$ s^{-1}. The rate of ligand substitution in $Al(H_2O)_6,F^{2+}$ is thus greater than the rate of exchange of solvent water with coordinated water in $Al(H_2O)_6^{3+}$.

Swaddle[26] has pointed out that the rate of ligand substitution can exceed the rate of exchange only if the ligand initiates the process, i.e., the substitution reaction proceeds by an associatively activated mechanism.[20,26] Thus, assuming a strongly solvated (two hydration layer) F^- leads directly to the conclusion that reaction 13 proceeds by an I_a mechanism.

An I_a mechanism for ligand substitution with F^- and an I_d mechanism for H_2O exchange requires that F^- is a "better" ligand than is H_2O toward $Al(H_2O)_6^{3+}$. Al^{3+} is a "hard" metal ion, and while it is uncertain which of the two ligands, H_2O or F^-, is "hardest" and therefore more nucleophilic toward Al^{3+}, a case could certainly be made for F^-. There may also be a steric effect by which F^- can attack the aluminum ion with less hinderance than H_2O. The latter agrees nicely with the postulate of Lo and Swaddle[21] that all octahedral complexes of trivalent metals undergo ligand substitution by an I_a mechanism unless the metal's ionic radius is less than about 0.60 Å, in which case the mechanism is I_d because of steric inhibition of I_a. Since the ionic radius of Al^{3+} is about 0.53 Å,[21] one might expect to see a change in mechanism from I_d to I_a if the steric strain in associative activation was reduced even a little. That seems to be the case in changing the ligand from H_2O to F^-. With an ionic radius of 1.33 Å,[27] F^- is slightly smaller than a water molecule with a radius of 1.38 Å.[28] Changing the ligand from H_2O to F^- appears to be sufficient to change the mechanism of the substitution reaction with $Al(H_2O)_6^{3+}$ from I_d to I_a.

The activation parameter values obtained for reaction 13 do not unambiguously indicate an I_a mechanism. In particular, $\Delta S^* = +82.9 \pm 21.7$ J mol^{-1} K^{-1} appears to be much too positive for an associatively activated mechanism. However, we believe that the positive ΔS^* value can be accounted for by the fact that the strongly hydrated fluoride ion must be considerably desolvated in order to form the activated complex.[17,29] This effect was shown quite clearly by ^{19}F NMR spectroscopy in aluminum–fluoride complexation where the ^{19}F resonance was shifted upfield upon complexation due to the dehydration of the fluoride ion accompanying Al–F bond formation.[30]

If this dehydration were occurring also in the activated complex, then the organization of solvent in the activated complex would be close to that of the final state, and the activated complex would be similar in size and charge to the end product of reaction. In that case the entropies of activation and reaction ought to be similar in magnitude and sign.[16,29] The standard entropy change for this reaction has been determined as $\Delta S° = +134$ J mol^{-1} K^{-1}.[31] However, since the activated complex in reaction 13 would have an additional water coordinated in an associatively activated mechanism, ΔS^* should be somewhat smaller than $\Delta S°$.[29] In fact, ΔS^* is 51 J mol^{-1} K^{-1} smaller than $\Delta S°$. In the reaction of $Fe(H_2O)_6^{3+}$ with SCN^-, which is thought to proceed by an I_a mechanism,[20,29] ΔS^* is 40 J mol^{-1} K^{-1} smaller than $\Delta S°$.[21] This is in good agreement with our results and lends further support to the assignment of an I_a mechanism for reaction 13.

Finally, it is noteworthy that ΔS^* values have been determined for the reactions of $Fe(H_2O)_6^{3+}$ with both F^- and HF. For the reaction with F^-, $\Delta S^* = +146 \pm 38$ J mol^{-1} K^{-1}, while, for the reaction with HF, $\Delta S^* = -100 \pm 13$ J mol^{-1} K^{-1}.[17] If both of these reactions proceed by I_a mechanisms as Hasinoff[32] and Lo and Swaddle[21] suggest, then the large positive ΔS^* for the reaction with F^- can only be accounted for by a significant dehydration of a strongly solvated F^-. As discussed above, a strongly solvated F^- leads directly to the assignment of an I_a mechanism for reaction 13 and explains the large positive ΔS^* value for that reaction as well.

In summary, we believe that a change in mechanism from I_d to I_a occurs in changing from $Al(H_2O)_5OH^{2+}$ to $Al(H_2O)_6^{3+}$ in reactions with F^-. A possible reason for such a change is that the higher charge density of $Al(H_2O)_6^{3+}$ increases the energy necessary to dissociate a bound water molecule, thus favoring an I_a mechanism for reaction 13.[32] It has been shown that an identical change in mechanism from I_d to I_a occurs in changing from $Fe(H_2O)_5OH^{2+}$ to $Fe(H_2O)_6^{3+}$ in reactions with Cl^-.[32]

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Registry No. $Al(H_2O)_6^{3+}$, 15453-67-5; $Al(H_2O)_5OH^{2+}$, 18499-02-0; F^-, 16984-48-8.

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