The Hydrolysis of Iridium(III)

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The hydrolysis of aquairidium(III) has been investigated at 5, 15, 25, and 35 °C in aqueous solutions of constant $[ClO_4]^-$ molality (1.05 mol kg^{-1}). A series of gravimetric titrations has been performed and the pH followed potentiometrically using hydrogen electrodes. The measurements are fully reversible even in the heterogeneous range and can be explained assuming the following equilibria:

$$[Ir(OH_2)_6]^{3+} \rightleftharpoons [Ir(OH_2)_5(OH)]^{2+} + H^+; \quad {}^*K_1 = [Ir(OH)][H^+][Ir]^{-1}$$

$$[Ir(OH_2)_5(OH)]^{2+} \rightleftharpoons [Ir(OH_2)_4(OH)_2]^+ + H^+; \quad {}^*K_2 = [Ir(OH)_2][H^+][Ir(OH)]^{-1}$$

$$[Ir(OH_2)_3(OH)_3](s) + 3H^+ \rightleftharpoons [Ir(OH_2)_6]^{3+}; \quad {}^*K_{s0} = [Ir][H^+]^{-3}$$

The individual equilibrium constants (using the molality scale) obtained at 25 °C (errors 1σ) are log $^*K_1 = -4.37 \pm 0.02$, log $^*K_2 = -5.20 \pm 0.15$, and log $^*K_{s0} = 10.22 \pm 0.05$. These results are compared with general predictions for the hydrolysis behaviour of aqua-cations.

OVER the last 25 years the hydrolysis reactions of cations have been thoroughly investigated.[1] The coexistence of monomeric and polymeric species has been demonstrated for most metal ions in acidic solutions. In a few cases, however, polymerization is so slow that the protolysis reactions (*i.e.* the consecutive stepwise deprotonations) can be followed separately. A good example of this behaviour is given by the inert hexa-aquachromium(III), where, as shown by Meyenburg *et al.*,[2] up to pH *ca.* 6 the experimental data can be explained by the equilibria (1)—(3). So far this seems to be the only case known where the time for equilibration is not markedly increased after the onset of metal hydroxide precipitation and where the heterogeneous reactions (3) involved are fully reversible. From this and additional arguments [2,3] it was concluded that chromium(III) hydroxide hydrate retained the original octahedra held together by hydrogen bonding in the solid compound.

$$[Cr(OH_2)_6]^{3+} \rightleftharpoons [Cr(OH_2)_5(OH)]^{2+} + H^+ \quad (1)$$

$$[Cr(OH_2)_5(OH)]^{2+} \rightleftharpoons [Cr(OH_2)_4(OH)_2]^+ + H^+ \quad (2)$$

$$[Cr(OH_2)_4(OH)_2]^+ \rightleftharpoons [Cr(OH_2)_3(OH)_3](s) + H^+ \quad (3)$$

A set of equilibria similar to (1)—(3) is expected to describe the protolysis behaviour of all sufficiently inert trivalent aqua-cations, regardless of other chemical differences. To test whether this simple kinetically based model also holds true for further cations, the recently prepared hexa-aquairidium(III) [4] has been studied by a series of potentiometric titrations. The composition of the products formed in the course of the protolysis processes over a range pH 1—11 was deduced and the corresponding equilibrium constants determined.[5] The relevant thermodynamic quantities were estimated from experiments at various temperatures.

EXPERIMENTAL

Reagents.—Sodium perchlorate was prepared from $HClO_4$ (70% p.a., Merck) and $Na_2[CO_3]$ (p.a., Merck) and carefully freed from protolytic impurities. The preparation of $[Ir(OH_2)_6]^{3+}$ stock solution was reported previously,[4] but since then the procedure has been slightly modified. It is extremely important to start with high-purity iridium compounds, *e.g.* $[NH_4]_2[IrCl_6]$ (puriss. Fa., Fluka). Use of lower grade $[NH_4]_2[IrCl_6]$ as starting material invariably gave unwanted products. Particularly critical is the quality of the cation-exchange resin. The best results were obtained with Dowex W 50X8 purchased from Fluka AG, Buchs SG, Switzerland. It was found that $[Ir(OH_2)_6]^{3+}$ stock solutions could be more readily prepared from the strong acid eluate obtained after the column treatment by reprecipitating iridium(III) hydroxide with NH_3 at pH *ca.* 6 instead of with Na[OH]. The solid product was thoroughly washed with $Na[ClO_4]$ (1.05 mol kg^{-1} water) and dissolved in a mixture of $HClO_4$ and $Na[ClO_4]$ (0.01 and 1.04 mol kg^{-1}). The total iridium content was analyzed by the method of Zinser and Page.[6] For preparing test solutions, S, measured quantities of this stock solution were diluted with $Na[ClO_4]$ (1.05 mol kg^{-1}). Alternatively, the strong acid eluate was evaporated at room temperature using a vacuum system (*ca.* 10^{-3} Torr).† Eventually a solid compound crystallizes out. The *X*-ray powder pattern of this substance was essentially the same as found for $Rh[ClO_4]_3 \cdot 6H_2O$;[7] hence the substance was concluded to be $Ir[ClO_4]_3 \cdot 6H_2O$.[8] After removal of most of the adhering $HClO_4$, this compound was dissolved in $Na[ClO_4]$ (1.05 mol kg^{-1}), analyzed, and diluted as before. Only reagent grade (Fa., Merck) substances and water, double distilled in an all-quartz apparatus, were used.

Apparatus.—Titrations were performed in a pear-shaped vessel containing *ca.* 10 cm^3 of solutions S, thermostatted to better than ±0.1 °C. Base solutions were transferred to the vessel with burettes. The test solutions were stirred with a stream of purified and presaturated hydrogen. The variation in pH was followed using cell (I) with a Wilhelm-type salt bridge.[9] The e.m.f.s of cell (I) were measured to ±0.1 mV with a digital pH-meter.

Pt, H_2 or glass electrode	test solution S	$Na[ClO_4]$ 1·05 mol kg^{-1}	NaCl 0·01 mol kg^{-1} $Na[ClO_4]$ 1·04 mol kg^{-1}	AgCl, Ag	(I)

Titration Procedure.—Solutions of the general composition $S_1\{[Ir^{III}]_T = B,\ [H^+] = H_0,\ [Na^+] = (1.05 - 3B - H_0),$

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† Throughout this paper: 1 Torr = (101 325/760) Pa.

and $[ClO_4^-] = 1.05$ mol kg^{-1}} were titrated with carbonate-free sodium hydroxide solutions $S_2\{[Na^+] = (1.05 + A)$, $[OH^-] = A$, and $[ClO_4^-] = 1.05$ mol kg$^{-1}\}$. Care was taken that H_0 and B were of the same order of magnitude. A value of E_0 for cell (I) was obtained from the first part of the titrations where protolysis of Ir^{III} was almost negligible. The data were treated by Gran's method.[10]

From the more alkaline parts of the titration curves, approximate protonation constants were calculated using the preliminary value for E_0. Then E_0 and the protonation constants were improved by an iterative procedure until they remained constant. In separate experiments, with hydrogen-ion concentrations up to 0.1 mol kg^{-1}, the junction-potential term E_j in the Nernst equation (4), where $k = RT \ln(10)/F$, showed a linear dependence on

$$E = E_0 + k \log [H^+] + E_j \qquad (4)$$

$[H^+]$. The numerical values were in a range as predicted by the Henderson equation[11] and as found in previous experiments.[1] Since in this work E_0 was evaluated from data at pH >2 it was comparatively insensitive to the value selected for E_j. Over the whole temperature range investigated the liquid-junction term was therefore described by (5) where $D = -65$ mV kg mol^{-1}. At every temperature investigated the respective ionization constants of water, K_w, in Na[ClO$_4$] (1.05 mol kg^{-1}) were determined from a series of strong acid–strong base titrations. The values obtained at 25 °C agreed to within 0.01 log units with results reported earlier.[12]

$$E_j = D[H^+] \qquad (5)$$

Calculation.—It should be emphasized that, as proposed[13] previously, molicity[13c] is a convenient quantity† for expressing compositions in the course of gravimetric titrations, the respective unit being mol kg^{-1} solution. Consequently this quantity was used for evaluating individual titrations; however, the final results were converted into molality, with mol kg^{-1} water as the unit consistent with S.I. The Gran equation, for a gravimetric titration of a strong acid with Na[OH], is (6) where M_1 and M_2 are the masses of water in solutions S_1 and S_2 respectively, $m^0{}_H$ is the initial molality of H^+ in S_1, $m^0{}_B$ is the molality of $[OH]^-$ in S_2, and m^0 is a standard value of molality equal to 1 mol kg^{-1} water. E_0 and $m^0{}_H$ were evaluated from equation (6) by a least-squares method * including an iterative correction for both E_j and the deprotonation of $[Ir(OH_2)_6]^{3+}$. The ligand number, Z, in this system is given by (7a) in

$$m^0(M_1 + M_2)10^{(E-E_j)/k} = 10^{E_0/k}(m^0{}_H M_1 - m^0{}_B M_2) \qquad (6)$$

$$Z = ([H^+] - [OH^-] - m_H)/m_{Ir} \qquad (7a)$$

acidic solutions and (7b) in basic solutions, where $m_H = -m_{OH}$ is the analytical excess of acid or base present and

$$Z = ([H^+] - [OH^-] + m_{OH})/m_{Ir} \qquad (7b)$$

m_{Ir}/mol kg^{-1} is the total content of Ir^{III}. The observed Z data at various pH and m_{Ir} were compared with model functions, and $(Z_{obs.} - Z_{calc.})^2$ was minimized to evaluate the respective equilibrium constants.

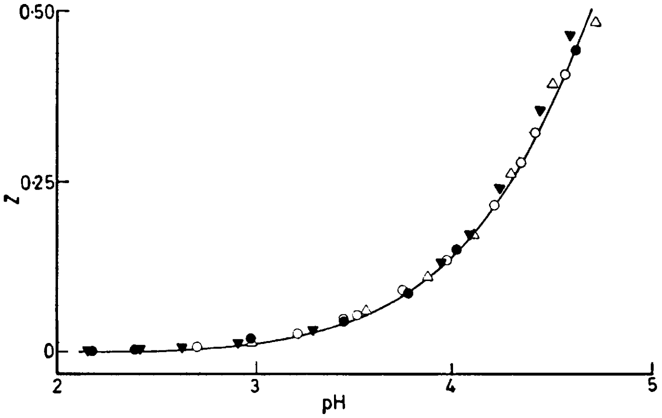

FIGURE 1 Protolysis of $[Ir(OH_2)_6]^{3+}$ at 5 °C, homogeneous range. $[Ir^{III}]_T = 1 \times 10^{-2}$ (●), 8×10^{-3} (▼), 5×10^{-3} (○), and 1×10^{-3} mol kg^{-1} (△). The solid line has been calculated with p*K_1 = 4.78 and p*K_2 = 5.63. Only every third data pair was plotted, the complete set of data being available on request

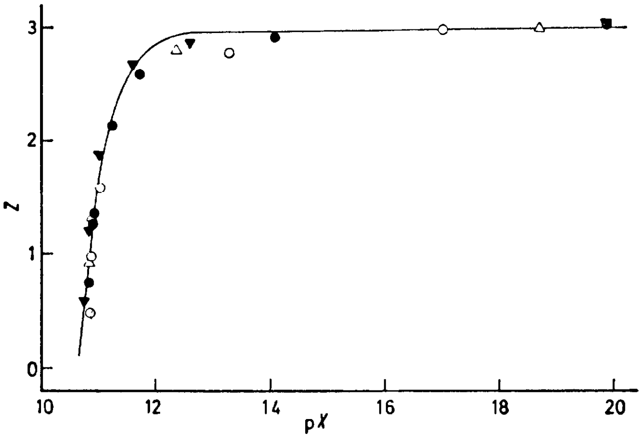

FIGURE 2 Protolysis of $[Ir(OH_2)_6]^{3+}$ at 5 °C, heterogeneous range. $[Ir^{III}]_T$ as in Figure 1. The solid line has been calculated with p*K_1 = 4.78, p*K_2 = 5.63, and log *K_{s0} = 11.10. Only every third pair was plotted, the complete set of data being available on request

RESULTS

A representative set of Z,pH data, obtained in the homogeneous range (pH 2.2—4.5), are shown in Figure 1. The absence of polynuclear species and solid iridium hydroxide is clearly demonstrated by the fact that Z is independent of m_{Ir}. The formation curve Z(pH) can be perfectly reproduced by assuming only two simultaneous protolysis reactions (8) and (9) with Z consequently given by (10a) and (10b). In equation (10a) and elsewhere, charges and coordinated water have been omitted for the sake of brevity. As shown in Figure 2, the Z function rises steeply for pH >4.5 (pX *ca.* 11) and levels off at $Z = 3$. Obviously, an additional heterogeneous reaction must be assumed with a mol ratio Ir : OH = 1 : 3 in the precipitate. With

$$[Ir(OH_2)_6]^{3+} \overset{*K_1}{\rightleftharpoons} [Ir(OH_2)_5(OH)]^{2+} + H^+ \qquad (8)$$

$$[Ir(OH_2)_5(OH)]^{2+} \overset{*K_2}{\rightleftharpoons} [Ir(OH_2)_4(OH)_2]^+ + H^+ \qquad (9)$$

$$Z = \frac{[Ir(OH)] + 2[Ir(OH)_2]}{[Ir] + [Ir(OH)] + [Ir(OH)_2]} \qquad (10a)$$

$$Z = \frac{*K_1[H^+]^{-1} + 2{*K_1}{*K_2}[H^+]^{-2}}{1 + *K_1[H^+]^{-1} + {*K_1}{*K_2}[H^+]^{-2}} \qquad (10b)$$

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† Molicity is defined as the amount (moles) of solute per mass (kilograms) of solution.

* A computer program written in BASIC is available from the authors on request.

equation (11), Z can be represented by (12a) and (12b) where $[Ir(OH)_3]$ refers to precipitated iridium(III) hydroxide

$$[Ir(OH_2)_3(OH)_3](s) + 3H^+ \xrightleftharpoons{*K_{so}} [Ir(OH_2)_6]^{3+} \quad (11)$$

$$Z = \frac{[Ir(OH)] + 2[Ir(OH)_2] + 3[Ir(OH)_3]}{[Ir] + [Ir(OH)] + [Ir(OH)_2] + [Ir(OH)_3]} \quad (12a)$$

$$Z = 3 - {*K_{so}}\{[H^+]^3(3 + 2{*K_1}[H^+]^{-1} + {*K_1}{*K_2}[H^+]^{-2})\}/m_{Ir} \quad (12b)$$

and should not be confused with the so far undetected, uncharged, dissolved complex species $[Ir(OH_2)_3(OH)_3]$.

Once $*K_1$ and $*K_2$ are determined it is possible to plot Z values in the heterogeneous range against the composite variable $X = [H^+]^3\ (3 + 2{*K_1}[H^+]^{-1} + {*K_1}{*K_2}[H^+]^{-2})m_{Ir}^{-1}$. The data for Z and pX (where p$X = -\log X$) fall on a single curve (Figure 2), thus the simple model of two homogeneous [(8) and (9)] and one heterogeneous (11) protolysis reactions seems to be correct. By this method, the equilibrium constants $*K_1$, $*K_2$, and $*K_{so}$ were determined at 5, 15, 25, and 35 °C and their numerical values are summarized in the Table. Plots of log K against $1/T$ were linear within the experimental errors, and $\Delta H^\ominus$ and $\Delta S^\ominus$ were calculated for reactions (8), (9), and (11). For further characterization, the iridium hydroxide precipitate was separated and analyzed by powder diffractometry. The powder patterns obtained were similar to that of chromium(III) hydroxide hydrate,[3] but due to their poor quality they could not be indexed properly. However, thermogravimetric and chemical analyses of this solid compound were consistent with the formula $[Ir(OH_2)_3(OH)_3]$.

Protolysis constants in the system iridium(III)–water in 1.05 mol kg^{-1} Na[ClO$_4$]

	θ_c/°C			
Mass-law expression	5	15	25	35
$-\log[Ir(OH)][H^+][Ir]^{-1}$	4.78	4.59	4.37	4.13
	(4.21)	(4.00)	(3.77)	(3.51)
$-\log[Ir(OH)_2][H^+][Ir(OH)]^{-1}$	5.63	5.27	5.20	5.08
	(5.14)	(4.77)	(4.69)	(4.56)
$-\log[Ir][H^+]^{-3}$	11.10	10.56	10.22	9.81
	(9.81)	(9.24)	(8.88)	(8.44)

Figures in parentheses refer to the ideal dilute solution.

DISCUSSION

It is interesting to compare the results of this work with the general predictions for the hydrolysis behaviour of aqua-cations as summarized by Baes and Mesmer.[1] For the initial hydrolysis step, the thermodynamic parameters in general depend linearly on the ratio of the cation charge z to the M–O interatomic distance d. The Ir–O distance ($d = 0.213$ nm) was taken from a recent compilation [14] of ionic radii; however, this value is only approximately known. According to Baes and Mesmer [1] it should be possible to calculate equilibrium constants and enthalpies and entropies of reactions analogous to (8) within uncertainties of ±1 log unit, ±8.4 kJ mol^{-1}, and 25 J K^{-1} mol^{-1} respectively, using equations (13)

$$\Delta{*H^\infty}_1 = A + Bzd^{-1} \quad (13)$$

$$\Delta{*S^\infty}_1 = C + Dzd^{-1} \quad (14)$$

and (14). In this context $\Delta{*H^\infty}_1$ and $\Delta{*S^\infty}_1$ refer to an ideal dilute solution, $A = 71.3$ kJ mol^{-1}, and $C = -140$ J K^{-1} mol^{-1} for cations with partly filled d orbitals, and $B = -1.92$ kJ nm mol^{-1} and $D = 14.6$ J nm K^{-1} mol^{-1}. The observed values for $*K_1$ were converted into the constant, $*K^\infty{}_1$ (valid in ideal dilute solution) employing equation (15), where s (0.511 kg$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ at 25 °C) is the Debye–Hückel limiting gradient and I is the ionic strength, usually set equal to the molality of the supporting 1 : 1 electrolyte. The parameter b (0.41 at $I = 1.05$ mol kg^{-1} Na[ClO$_4$]) was taken to be temperature independent and equal to the value [1] listed for $[Cr(OH_2)_5(OH)]^{2+}$ since both the acidity and interatomic M–O distance of Cr^{3+}(aq) and Ir^{3+}(aq) are similar. The results obtained from (13) and (14) agree, within the limits predicted, with the experimentally observed values given in parentheses: $-\log {*K^\infty}_1 = 4.33$ (3.77) at 25 °C, $\Delta{*H_1} = 44.3$ (38.2) kJ mol^{-1}, and $\Delta{*S_1} = 65.6$ (56.2) J K^{-1} mol^{-1}. Obviously, the concepts inherent in (13) and (14) allow a fairly good prediction for the initial hydrolysis steps. Iridium(III), a cation which had not been studied when the initial correlation was set up and thus did not influence the constants A—D, shows a very close fit.

$$\log {*K^\infty}_1 = \log {*K_1} + 4sI^{\frac{1}{2}}(1 + I^{\frac{1}{2}})^{-1} - bI \quad (15)$$

An equation analogous to (15) has been used to calculate log $*K^\infty{}_2$ (Table). Again b (0.01 at $I = 1.05$ mol kg^{-1} Na[ClO$_4$]) was taken to be equal to the value [1] given for $[Cr(OH_2)_4(OH)_2]^+$. Moreover, Baes and Mesmer [1] have shown that in general the solubility constant of the stable hydroxide is correlated to the first protolysis constant such that in most cases the quantities $K^\infty = ({*K^\infty}_1)^z \cdot {*K^\infty}_{so}$ for reactions (16) fall within ±3 log units of the mean value log $K^\infty = -5.6$. To test this correlation the observed solubility constant of $[Ir(OH_2)_3(OH)_3]$(s) was extrapolated to zero ionic strength with equation (17), where b (−0.2 at $I = 1.0$ mol kg^{-1} Na[ClO$_4$]) is the same as for chromium hydroxide. A comparatively high value of log $K^\infty = -2.43$ was obtained at 25 °C. This reflects the general tendency of inert trivalent aqua-cations to hydrolyze considerably until precipitation begins.[5] Labile cations exhibit a conspicuously different behaviour in that only a small fraction of the hydrolyzed species can exist in equilibrium with the stable solid phase; however, usually supersaturation occurs. With inert trivalent aqua-cations, simple, reversible, deprotonation reactions eventually lead to a stable solid product, whereas labile aqua-cations often form polynuclear hydroxo-complexes which do not fit into the regular arrangement of lattice sites. Consequently, hydrolysis of labile cations usually results in amorphous hydroxides and it takes a long time for the final heterogeneous equilibrium to be attained.

$$[M(OH)_z](s) + (z - 1)M^{z+} \rightleftharpoons z[M(OH)]^{(z-1)+} \quad (16)$$

$$\log {*K^\infty}_{so} = \log {*K_{so}} - 6sI^{\frac{1}{2}}(1 + I^{\frac{1}{2}})^{-1} - bI \quad (17)$$

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