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Kinetics of Aquation of Aquopentachloroiridate(III) and Chloride Anation of Diaquotetrachloroiridate(III) Anions[1a,b]

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The kinetics of the reactions $Ir(OH_2)Cl_5^{-2} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Ir(OH_2)_2Cl_4^- + Cl^-$ were investigated. Aquation of $Ir(OH_2)Cl_5^{-2}$ was studied at 40–65° in 1.0–2.5 F $HClO_4$. At 50.00° $k_2 = (1.26 \pm 0.05) \times 10^{-5}$ sec.$^{-1}$, essentially independent of $(Ir(OH_2)Cl_5^{-2})_0$ from 4.86 to 9.66 mF and of (H^+) from 1.02 to 2.55 F (μ = 3.72–3.75, $NaClO_4$). $E_a = 29.4 \pm 0.6$ kcal. and log $pZ = 15.1 \pm 0.4$; from these data k_2 at 25° is calculated to be $(8 \pm 7) \times 10^{-7}$ sec.$^{-1}$. Light has no apparent effect on the aquation rate. Chloride anation of $Ir(OH_2)_2Cl_4^-$ was studied in the absence of light at 25–50° in 0.15–2.5 F H^+ (μ = 2.22–3.70, NaCl + $NaClO_4$). At 50.00° and 2.50 F H^+ the rate law was found experimentally to be $-d(Ir(OH_2)_2Cl_4^-)/dt = k_{-2}(Ir(OH_2)_2Cl_4^-)(Cl^-)$, where (Cl^-) is taken as the Cl^- formality (0.3–0.9) and $k_{-2} = (6.7 \pm 0.4) \times 10^{-5}$ M^{-1} sec.$^{-1}$, independent of μ. $E_a = 27.8 \pm 0.6$ kcal. and log $pZ = 14.6 \pm 0.4$ (M^{-1} sec.$^{-1}$); at 24.95° $k_{-2} = (1.77 \pm 0.06) \times 10^{-6}$ M^{-1} sec.$^{-1}$. Decrease of (H^+) from 2.5 to 0.15 F decreases k_{-2} at 50° by 22 ± 2%. The aquation rate constant for $Ir(OH_2)_2Cl_4^-$ in 2.5 F $HClO_4$–1.2 F $NaClO_4$ is estimated to be $(0.29 \pm 0.01) \times 10^{-5}$ sec.$^{-1}$ at 50.00°. The previously unreported complexes $Ir(OH_2)_2Cl_4^-$, $Ir(OH_2)_2Cl_4$, $Ir(OH_2)_3Cl_3$, and $Ir(OH_2)_3Cl_3^+$ were characterized (geometrical configurations unknown) and their visible absorption spectra obtained. At 25° the acid dissociation constants of $Ir(OH_2)_2Cl_4^-$ are $pK_a = 8.5 \pm 0.4$ and 10.1 ± 0.5. At 25° $Ir(OH_2)Cl_5^{-2} = Ir(OH_2)Cl_5^- + e^-$, $E° \approx -1.0$ volt in 0.2 F HNO_3, $Ir(OH_2)_2Cl_4^- = Ir(OH_2)_2Cl_4 + e^-$, $E° \approx -1.2$ volts in 0.4 F HNO_3; these Ir(IV) species are relatively strong oxidants.

Few papers have appeared in the chemical literature on substitution reactions of inert 4d and 5d metal complexes. In extension of an investigation[2] of the aquation of hexachloroiridate(III) and chloride anation[3] of aquopentachloroiridate(III) anions

$$IrCl_6^{-3} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Ir(OH_2)Cl_5^{-2} + Cl^- \qquad (1)$$

we report here a study of the kinetics of aquation of aquopentachloroiridate(III) and chloride anation of diaquotetrachloroiridate(III) anions

$$Ir(OH_2)Cl_5^{-2} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Ir(OH_2)_2Cl_4^- + Cl^- \qquad (2)$$

together with preliminary observations on the rate of aquation of diaquotetrachloroiridate(III) anion to triaquotrichloroiridium(III). The visible absorption spectra of the previously unreported diaquo and triaquo species, both in the iridium(III) and iridium(IV) oxidation states, were established in acid solutions.

Experimental

Ammonium Aquopentachloroiridate(III).—Commercial $(NH_4)_2IrCl_6$ (Fairmount Chemical Co., Inc., Newark, N. J.), found to contain 0.6% Pt, 0.3% Pd, and 0.4% Rh, was purified essentially by the method of Woo and Yost,[4] with the addition of a chromatographic separation of Ir and Pt.[5,6] Spectrographic analysis of the purified compound showed 0.15% Rh and no other Pt metals. This purified $(NH_4)_2IrCl_6$ was used to prepare $(NH_4)_2Ir(OH_2)Cl_5$ by the method of Sloth and Garner.[7]

Anal. Calcd. for $(NH_4)_2Ir(OH_2)Cl_5$: Ir, 45.37; Cl as HCl, 25.11; Cl as NH_4Cl, 16.74; N, 6.61; reduction equivalents per Ir, 1.00. Found: Ir, 45.15; Cl as HCl, 25.10; Cl as NH_4Cl, 15.80; N, 6.54; reduction equivalents per Ir, 1.01.

Sodium Hexachloroiridate(III).—This compound was prepared by the method of Poulsen and Garner[2] for use as a standard in testing analytical procedures.

Anal. Calcd. for Na_3IrCl_6: Ir, 40.56; Cl as HCl, 22.44; Cl as NaCl, 22.44. Found: Ir, 41.34; Cl as HCl, 22.02; Cl as NaCl, 22.02.

Triaquotrichloroiridium(III).—A mixture of this compound and $Ir(OH_2)_2Cl_4^-$ was prepared by boiling for 2 min. a solution of *ca.* 1 g. of $(NH_4)_2Ir(OH_2)Cl_5$ in 10 ml. of 1 F $HClO_4$. After oxidation of Ir species to Ir(IV) with Cl_2 for 15 min. at *ca.* 25°, the solution was chromatographed on a NO_3^- Dowex AG 1-X8 column (see Chromatography of Aquation Solutions). The neutral $Ir(OH_2)_3Cl_3$ (in the Ir(III) state owing to quantitative reduction on the resin column) was separated free from other Ir species by elution with 0.001 F $HClO_4$, discarding the first 10 ml. and collecting the next 30 ml. of effluent. To remove cationic complexes possibly present (none was found) the 30-ml. effluent was passed through a Na^+ Dowex AG 50W-X8 column, 100–200 mesh, giving a solution *ca.* 1 mF in $Ir(OH_2)_3Cl_3$. A Cl/Ir atom ratio of 2.99 was found. The visible absorption spectrum in 2.5 F $HClO_4$–1.2 F $NaClO_4$ did not change when the solution was made 60 mF in H_2O_2, showing further that the complex was all in the Ir(III) state. The geometrical configuration was not established.

Triaquotrichloroiridium(IV) Cation.—This complex was obtained by oxidation of $Ir(OH_2)_3Cl_3$ solutions with Cl_2 at *ca.* 25°. The configuration was not determined. The complex (in 0.001 F $HClO_4$) was completely adsorbed on a 1-cm. diameter × 10-cm. column of Na^+ Dowex AG 50W-X8, 100–200 mesh, prefilled with 0.001 F $HClO_4$, showing the complex to be cationic.

Diaquotetrachloroiridate(III) Anion.—The complex was prepared in solution and chromatographed on a NO_3^- Dowex AG 1-X8 column (see Triaquotrichloroiridium(III)); triaquo species were eluted with 100 ml. of 0.001 F $HClO_4$, then the diaquo complex (in the Ir(III) state owing to quantitative reduction on the resin column) was eluted with 0.3 F HNO_3, discarding the first 50 ml. and collecting the next 100 ml. of effluent (*ca.* 10 mF in $Ir(OH_2)_2Cl_4^-$). A Cl/Ir atom ratio of 3.99 and 1.00 reduction equivalent per Ir were found for this complex (unknown configu-

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[1] (a) Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University; (b) abstracted in part from the Ph.D. dissertation of James C. Chang, University of California, Los Angeles, Aug. 1964.

[2] I. A. Poulsen and C. S. Garner, *J. Am. Chem. Soc.*, **84**, 2032 (1962).

[3] Anation is the replacement of ligand water in a complex by an anion.

[4] S. C. Woo and D. M. Yost, *J. Am. Chem. Soc.*, **53**, 884 (1931).

[5] K. A. Kraus, F. Nelson, and G. W. Smith, *J. Phys. Chem.*, **58**, 11 (1954).

[6] D. D. Busch, J. M. Prospero, and R. A. Naumann, *Anal. Chem.*, **31**, 884 (1959).

[7] E. N. Sloth and C. S. Garner, *J. Chem. Phys.*, **22**, 2064 (1954).

ration). Further proof that the complex was all in the Ir(III) state was supplied by noting that its visible absorption spectrum in 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$ did not change on making the solution 60 m*F* in H_2O_2.

Diaquotetrachloroiridium(IV).—This neutral complex was obtained in solution by oxidation of solutions of $Ir(OH_2)_2Cl_4^-$ with Cl_2 at *ca.* 25°. The geometrical configuration has not been established. The complex is readily reduced in acid solution by H_2O_2.

Sodium Perchlorate.—Commercial C.P. $NaClO_4$ was found to contain oxidizing impurities, so $NaClO_4$ was made by neutralizing C.P. Na_2CO_3 with $HClO_4$ (J. T. Baker Analyzed).

Other Chemicals.—All other chemicals were C.P. or reagent grade. The water was doubly distilled, then passed through a mixed-bed cation–anion resin and monitored for purity by electrical conductivity.

Chemical Analyses.—Weighed portions of solid Ir compounds were analyzed[2,7] by reduction to metallic Ir, alkali or ammonium chloride, and HCl by H_2 at 500–600° for 3 hr.

Iridium in solution was determined as $IrCl_6^{-2}$. A 4- to 10-ml. aliquot containing 0.4–0.1 μg.-atom of Ir was heated with 10 ml. of 2.5 *F* LiCl–0.1 *F* $HClO_4$ at *ca.* 100° for *ca.* 1 hr. (until the appearance of solids) to Cl^- anate all species quantitatively to $IrCl_6^{-3}$ and/or $IrCl_6^{-2}$. The mixture was made up to 50.00 ml. with Cl_2-saturated 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$, and the absorbancy due to $IrCl_6^{-2}$ was measured at 488 mμ against an identical reagent blank (without Ir complex) as reference solution in matched 10.00-cm. Pyrex cells, using a Beckman DU spectrophotometer. The molar absorbancy index of the $IrCl_6^{-2}$ thus produced in this medium was established at 25° to be 4060 M^{-1} cm.$^{-1}$ (standard deviation from 81 values, 1.2%), using pure Na_3IrCl_6 and $(NH_4)_2Ir(OH_2)Cl_5$ as standards.

Ligand Cl was determined as follows. A slight excess of 1 *F* NaOH was added to a 10-ml. aliquot of a solution of the diaquo or triaquo complex, and the mixture was heated at *ca.* 100° for 30 min. After the solution was cooled, *ca.* 30 mg. of $Al_2(SO_4)_3$ and enough 0.3 *F* HNO_3 were added (until the solution containing bromophenol blue indicator turned yellow) to precipitate the colloid formed, which was filtered off. The combined filtrate and washings was then titrated for Cl^- by the method of Clarke.[8]

The number of reduction equivalents per formula weight of $(NH_4)_2Ir(OH_2)Cl_5$, and of $Ir(OH_2)_2Cl_4^-$ in the resin-column effluents, was determined by potentiometric titration of O_2-free solutions of each complex with standard 0.01 *N* $(NH_4)_2Ce(NO_3)_6$ (1 *F* in HNO_3), using a Rh foil electrode, a saturated calomel electrode, and a Radiometer PHM-4c meter as a potentiometer. Essentially identical results were obtained when 0.01 *N* $KMnO_4$ was used in the titrations.

Oxidation Potentials.—Approximate values of the standard oxidation potentials $E°$ for the reversible couples $Ir(OH_2)Cl_5^{-2} = Ir(OH_2)Cl_5^- + e^-$ (in 0.2 *F* HNO_3) and $Ir(OH_2)_2Cl_4^- = Ir(OH_2)_2Cl_4 + e^-$ (in 0.4 *F* HNO_3) were obtained from potentiometric titration curves at 25° by subtracting the e.m.f. corresponding to half-oxidation of the complex from $E°$ for the saturated calomel electrode (-0.24 volt). Ignoring presumably small liquid-junction potentials, we obtain $E° = -1.0$ and -1.2 volts, respectively.[9]

Kinetic Runs.—In aquation runs weighed amounts of $(NH_4)_2Ir(OH_2)Cl_5$ were dissolved in O_2-free stock solvents of $HClO_4$ and $NaClO_4$. In chloride anation runs, $Ir(OH_2)_2Cl_4^-$ in 0.3 *F* HNO_3 was mixed with stock solvents of $HClO_4$, NaCl, and $NaClO_4$ to the (H^+), (Cl^-), and μ desired. The initial concentrations of $Ir(OH_2)Cl_5^{-2}$ and $Ir(OH_2)_2Cl_4^-$ were determined by the LiCl anation method (see Chemical Analyses).

Reaction solutions (7-ml. portions) were sealed by torch in Pyrex ampoules, which were wrapped in Al foil to exclude light (except when the effect of light was to be studied), and the ampoules were placed in thermostated baths at 24.95 ± 0.01, 40.00 ± 0.02, 50.00 ± 0.10, and 65.00 ± 0.15°. Zero reaction time was taken 5 min. later, which time was found adequate for the solution to heat up to bath temperature. Ampoules were removed at known times, quenched in ice, and the contents analyzed by methods described below.

Chromatography of Aquation Solutions.—A 5.00-ml. aliquot of an aquation solution, after addition of 1 ml. of 0.05 *F* $KMnO_4$ to oxidize the Ir(III) species to Ir(IV)[10] following addition of 1 ml. of 0.05 *F* $Mn(NO_3)_2$ to prevent oxidation of Cl^-, was passed by gravity through a 1 × 24 cm. bed of NO_3^- Dowex AG 1-X8, 100–200 mesh, in a jacketed glass column. The effluent was collected in a 50-ml. volumetric flask. Ionic Cl^- was eluted with 0.3 *F* HNO_3, the effluent being collected in the same volumetric flask until a total of 50 ml. was collected. After mixing, an aliquot of this effluent was adjusted to pH 3 with solid Na_2CO_3 followed by 0.3 *F* HNO_3 (using bromophenol blue indicator), then titrated with standard 0.01 *F* $Hg(NO_3)_2$ by the Clarke method[8] to determine the amount of Cl^- released in the aquation reaction.

An additional 150 ml. of 0.3 *F* HNO_3 was passed through the column to elute the reaction product, tests having established that its elution was completed by this volume of eluent without stripping any oxidized unreacted reactant off the column. Then the column was heated by circulating H_2O at 40° through the surrounding jacket, and the oxidized unreacted reactant was eluted with 300 ml. of 1 *F* $NaClO_4$ at a flow rate of *ca.* 1.5 ml./min. The amount of Ir in this effluent was determined by the LiCl anation method.

Elution of $Ir(OH_2)Cl_5^-$ from NO_3^- Dowex AG 1-X8 was not quantitative; however, the per cent recovery was found constant for a given lot of resin.[11] In following the aquation by the determination of unreacted reactant, a standardized lot of Dowex AG 1-X8, which gave 90.0 ± 1.0% recovery of $Ir(OH_2)Cl_5^-$, was used.

Spectrophotometry.—Optical absorbancies of aquation run aliquots were measured at 330 and 380 mμ with a Beckman DU spectrophotometer at *ca.* 25° using matched 1.000-cm. quartz cells. Then 1- or 2-ml. aliquots of reaction solution were diluted to 25 ml. with Cl_2-saturated 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$ and measured at 485 and 500 mμ. In Cl^- anation runs aliquots were measured spectrophotometrically only after oxidation with Cl_2. In all these spectrophotometric measurements the reference cell was filled with an identical solution except for the absence of Ir species.

Molar absorbancy indices of the Ir(III) complexes were obtained at 25° in O_2-free 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$. Immediately after these solutions were prepared, the spectra were also measured on a Cary Model 11 recording spectrophotometer, using matched 1.000-cm. quartz cells or 10.00-cm. Pyrex cells. The spectra of these species in the Ir(IV) state were measured 10 min. after diluting a suitable aliquot of each solution of Ir(III) complex to 25 ml. with Cl_2-saturated 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$.

During the aquation and anation runs the spectra of run solutions were scanned at various reaction times on a Cary Model 11 recording spectrophotometer at *ca.* 25° both before and after oxidation with Cl_2 to search for isosbestic points.

Results

Spectra of New Iridium Complexes.—Figure 1 exhibits the visible and near-ultraviolet absorption spectra of the new Ir(III) complexes $Ir(OH_2)_2Cl_4^-$ and $Ir(OH_2)_3Cl_3$, together with the spectra of $IrCl_6^{-3}$ and $Ir(OH_2)Cl_5^{-2}$ in 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$; the spectrum of $Ir(OH_2)Cl_5^{-2}$ is in reasonable agreement with that reported by Poulsen and Garner[2] in water (their

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(8) F. E. Clarke, *Anal. Chem.*, **22**, 553 (1950).

(9) As used here, a negative value of $E°$ means that the reduced form of the couple is thermodynamically a poorer reducing agent than H_2 in the standard H_2, H^+ couple.

(10) As found by Poulsen and Garner,[2] chromatography without oxidation of the Ir(III) species was unsuccessful because of the low affinity of Ir(III) species for the ion-exchange resin and because of the presence of large amounts of ClO_4^- in the solutions being chromatographed.

(11) Attempts to purify the resin or to pretreat with Ir species were unsuccessful.

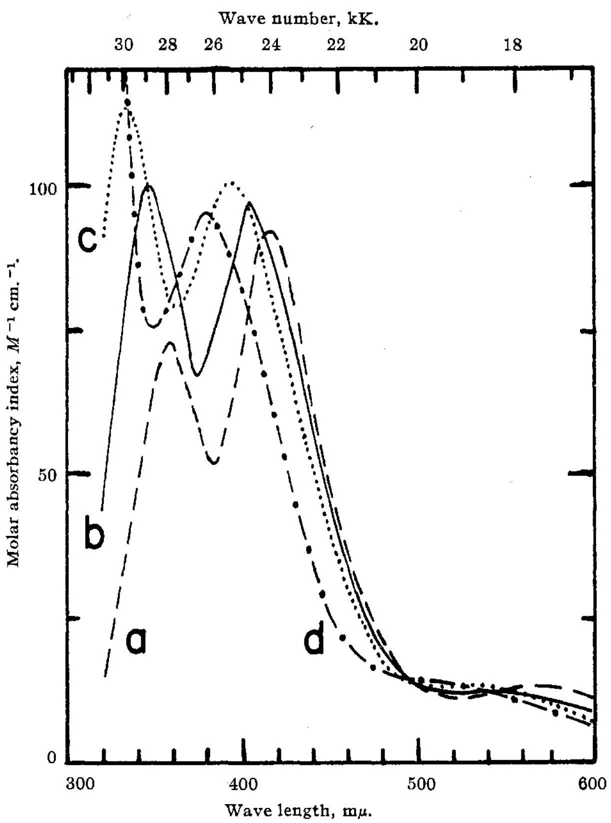

Figure 1.—Visible absorption spectra of hexachloro and aquochloro complexes of iridium(III) in 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$ at 25°: a, $IrCl_6^{-3}$ (ref. 2); b, $Ir(OH_2)Cl_5^{-2}$; c, $Ir(OH_2)_2Cl_4^-$; d, $Ir(OH_2)_3Cl_3$.

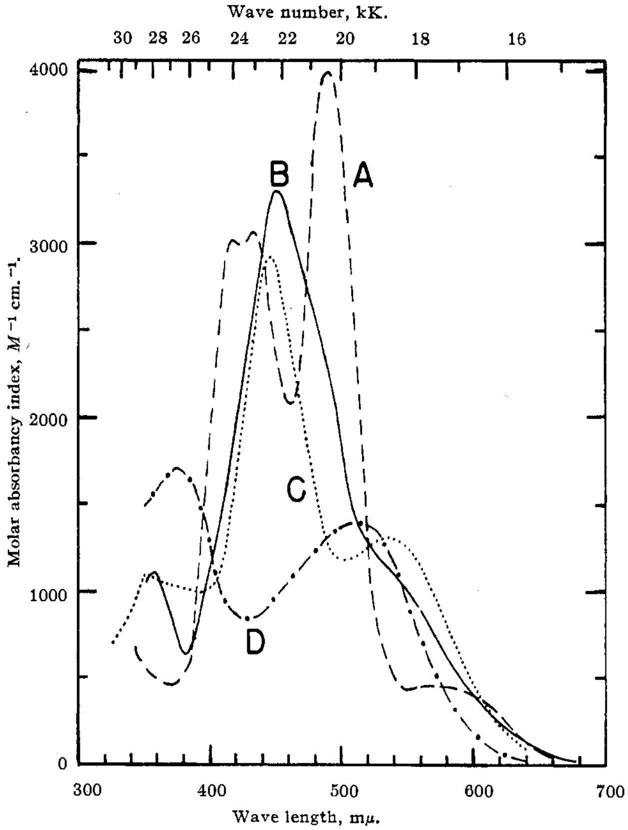

Figure 2.—Visible absorption spectra of hexachloro and aquopentachloro complexes of iridium(IV) in Cl_2-saturated 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$ at 25°: A, $IrCl_6^{-2}$ (ref. 2); B, $Ir(OH)_2Cl_5^-$; C, $Ir(OH_2)_2Cl_4$; D, $Ir(OH_2)_3Cl_3^+$.

TABLE I

ABSORPTION MAXIMA AND MINIMA OF Ir(III) AND Ir(IV) CHLOROAQUO COMPLEXES IN 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$[a] AT 25°

Complex	λ, mμ	a_M, M^{-1} cm.$^{-1}$[b]
$Ir(OH_2)_2Cl_4^-$	333 (max.)	113
	360 (min.)	78.4
	392 (max.)	100
	510 (min.)	13.0
	530 (max.)	13.1
$Ir(OH_2)_2Cl_4$	350 (max.)	1090
	395 (min.)	983
	445 (max.)	2920
	500 (min.)	1170
	535 (max.)	1310
$Ir(OH_2)_3Cl_3$	350 (min.)	75.0
	378 (max.)	95.0
$Ir(OH_2)_3Cl_3^+$	373 (max.)	1700
	425 (min.)	830
	510 (max.)	1400

[a] Solutions of Ir(IV) complexes and their reference solutions were saturated with Cl_2. [b] The molar absorbancy index a_M, sometimes called the molar extinction coefficient ε, is related to the optical absorbancy *A* by $A = \log (I_0/I) = a_M cd$ at a given wave length, where *c* is the molar concentration of the absorbing species and *d* is the optical path length in cm.

spectrum shows a peak at 553 mμ instead of 540 mμ) and by Jørgensen.[12] Spectra of the corresponding Ir(IV) complexes are shown in Figure 2 in the same medium saturated with Cl_2 (the spectra are corrected for absorption by Cl_2); the spectrum of $Ir(OH_2)Cl_5^-$ agrees well with that reported by Poulsen and Garner[2] except the minimum lies 4 mμ higher than they reported. The absorption maxima and minima are given in Table I.

Product of Primary Aquation of $Ir(OH_2)Cl_5^{-2}$.—This product was identified, by spectrum, as $Ir(OH_2)_2Cl_4^-$ which appeared in the 0.3 *F* HNO_3 effluent. The change in the spectrum of the aquation reaction solution corresponds to a change of $Ir(OH_2)Cl_5^{-2}$ to $Ir(OH_2)_2Cl_4^-$ up to about 40% reaction, since three definite isosbestic points were observed at 399–400, 363–364, and 342–343 mμ with molar absorbancy indices of 97.8 ± 1.0, 75.4 ± 0.3, and 100 ± 0.7 M^{-1} cm.$^{-1}$, respectively (theoretical, from Figure 1, 402, 364, and 345 mμ with a_M of 96.8, 79.0, and 99.5 M^{-1} cm.$^{-1}$, respectively). In addition somewhat less definite isosbestic points appeared near 560 and 500 mμ, in approximate agreement with the theoretical predictions (567 and 500 mμ), but low absorbancies made these two isosbestic points uncertain. Two definite isosbestic points were observed in the spectrum of the oxidized aquation solution (after diluting an aliquot with Cl_2-saturated 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$) at 518–523 and 395–398 mμ with a_M of 1270 ± 10 and 970 ± 20 M^{-1} cm.$^{-1}$, respectively (theoretical, from Figure 2, 520 and 395 mμ with a_M of 1260 and 980 M^{-1} cm.$^{-1}$, respectively). There also appeared to be an isosbestic point at 615–620 mμ (theoretical, 615 mμ), but low absorbancies made this uncertain; two isosbestic points observed below 395 mμ (theoretical, 359 and 353 mμ) were very

[12] C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 151 (1957).

TABLE II
FIRST-ORDER RATE CONSTANTS FOR AQUATION OF $Ir(OH_2)Cl_5^{-2}$ IN INITIALLY Cl^--FREE $HClO_4$ SOLUTIONS

Run no.	Temp., °C.	C_0, mF	(H^+), F	μ,[a] F	10^5k_2, sec.$^{-1}$
12	40.00	9.50	2.55	3.75	0.40 ± 0.02[c]
5	50.00	4.86	2.55	3.75	1.43 ± 0.06[d]
					1.56 ± 0.14[e]
					1.37 ± 0.12[f]
1	50.00	9.28	2.55	3.75	1.26 ± 0.07[c]
					1.23 ± 0.03[g]
2	50.00	9.52	2.55	3.75	1.27 ± 0.03[c]
4	50.00	9.64	2.55	3.75	1.38 ± 0.02[c]
3	50.00	9.66	2.55	3.75	1.29 ± 0.04[c]
9	50.00	9.88	2.55	3.75	1.34 ± 0.02[c,i]
7	50.00	5.53	1.02	3.72	1.18 ± 0.05[d]
					1.20 ± 0.06[e]
					1.35 ± 0.03[f]
					1.48 ± 0.03[h]
6	50.00	10.8	1.02	3.72	1.23 ± 0.01[c]
8	50.00	10.6	1.02	2.22	1.87 ± 0.04[c]
					1.80 ± 0.07[g]
11	65.00	5.14	2.55	3.75	11.5 ± 0.3[d]
					11.5 ± 0.2[e]
					11.9 ± 0.2[f]
					13.0 ± 0.5[h]
10	65.00	9.50	2.55	3.75	12.7 ± 0.4[c]

[a] Ionic strength adjusted with $NaClO_4$. [b] Obtained from a least-squares analysis; errors given are standard deviations. [c] Cl^- release. [d] Spectrophotometrically, 330 mμ. [e] Spectrophotometrically, 380 mμ. [f] Spectrophotometrically on oxidized aliquot, 485 mμ. [g] Chromatographically separated unreacted reactant. [h] Spectrophotometrically on oxidized aliquot, 500 mμ. [i] Reaction under 100-watt incandescent light 10 in. distant.

uncertain because of interference from Cl_2 in the solution.

Rate of Aquation of $Ir(OH_2)Cl_5^{-2}$.—Titrimetric determinations of Cl^- released in the aquation of $Ir(OH_2)Cl_5^{-2}$ (forward reaction 2) allowed computation of the molar concentration C of reactant at reaction time t in terms of its initial concentration C_0: $C = C_0 - (Cl^-)$. Plots of ln (C_0/C) *vs.* t gave good straight lines up to 60% aquation, the slopes of which gave k_2. These values of k_2 are given in column 6 (footnote *c* values) of Table II.

Determinations of the concentration of chromatographically separated unreacted $Ir(OH_2)Cl_5^{-2}$ at time t permitted the construction of ln (C_0/C) *vs.* t plots; these were linear up to 60% aquation. Values of k_2 obtained by this method (column 6, footnote *g* values, Table II) are in good agreement with the more accurate values derived from Cl^- release data.

The rate was also followed spectrophotometrically. Although the absorbancy differences between the spectra of $Ir(OH_2)Cl_5^{-2}$ and $Ir(OH_2)_2Cl_4^-$ (curves b and c, Figure 1) are not large, those at 330 and 380 mμ are sufficiently large for the measurement of the reaction rate. The spectra of the oxidized species $Ir(OH_2)Cl_5^-$ and $Ir(OH_2)_2Cl_4$ are more different (Figure 2, curves B and C), but in view of the partial interference from Cl_2 at wave lengths below *ca.* 400 mμ the differences are large enough for accurate spectrophotometric measurements of the reaction rate only in the region 460–500 mμ; 485 and 500 mμ were chosen. In terms of the optical absorbancies A_0, A, and A_∞ (at a given wave length) at time zero, time t, and at 100% aquation of the first ligand chloride, respectively, the first-order rate equation is

$$\ln\ [(A_0 - A_\infty)/(A - A_\infty)] = k_2t \qquad (3)$$

Plots of this logarithmic function of the absorbancies at 330, 380 (for the unoxidized aliquots), 485, and 500 mμ (for the oxidized aliquots) *vs.* t gave good straight lines up to *ca.* 40% aquation for runs with Cl^- initially absent. Average values of a_M for $Ir(OH_2)_2Cl_4^-$ and $Ir(OH_2)_2Cl_4$ at these wave lengths were used to calculate A_∞. Spectrophotometric values of k_2 are given in column 6 (footnote *d*, *e*, *f*, and *h* values) of Table II; actual errors for these k_2 values are probably 2–4 times greater than the least-squares errors given because of errors in the A_∞ values. The spectrophotometric values of k_2 are generally in satisfactory agreement with the more accurate values obtained by the other two methods. In run 7 there is a spread of 25% between the extreme values obtained at different wave lengths for reasons which are not clear; the average of these values is, however, about the same as the values obtained from the Cl^- release data at the same acidity.

The values of k_2 at 50° and at constant ionic strength (3.72–3.75) are reasonably independent of a 2.0-fold change in $(Ir(OH_2)Cl_5^{-2})_0$ (runs 1–5) and of a 2.5-fold change in (H^+) (runs 1–7); a weighted average of $(1.26 \pm 0.05) \times 10^{-5}$ sec.$^{-1}$ may be taken for k_2 over this range ($t_{1/2}$ = 15.3 hr.). Decrease of μ from 3.75 to 2.22 increased k_2 by a factor of about 1.4 (runs 1–8); a similar, somewhat larger, effect was observed[2] for aquation of $IrCl_6^{-3}$ at 50°. The effect may be associated with ion-pair formation, but no known theory can be applied to reactions at such high ionic strengths. Use of ionic strengths sufficiently low to allow use of the extended Debye–Hückel theory would require much lower hydrogen ion concentrations and were avoided because of the possibility of olation reactions. Light of the intensity used has no significant effect on the aquation rate (runs 1–5, 9).

The Arrhenius activation energy E_a for the aquation of $Ir(OH_2)Cl_5^{-2}$ was obtained from a plot of log k_2 *vs.* $1/T$ for the titrimetric values of Table II; this plot was linear and gave $E_a = 29.4 \pm 0.6$ kcal., with log $pZ = 15.1 \pm 0.4$ (sec.$^{-1}$).

Rate of Cl^- Anation of $Ir(OH_2)_2Cl_4^-$.—The anation rate was followed only spectrophotometrically inasmuch as the anation was necessarily carried out at Cl^- concentrations very much larger than the initial concentration C_0 of $Ir(OH_2)_2Cl_4^-$ reactant and Cl^- uptake could not be measured accurately. Even by a spectrophotometric method it was feasible to follow the anation only by absorbancy measurements of Cl_2-oxidized aliquots of the reaction solution since the $Ir(OH_2)Cl_5^{-2}$ formed in the anation of $Ir(OH_2)_2Cl_4^-$ is itself anated to $IrCl_6^{-3}$ at a comparable rate, and this $IrCl_6^{-3}$ was partly oxidized to $IrCl_6^{-2}$ (apparently by traces of O_2 in the 0.3 F HNO_3 effluent containing the diaquo complex in its synthesis and separation); the $IrCl_6^{-2}$ by-product absorbs strongly over much of the visible and near-ultraviolet regions and would mask the

TABLE III

SECOND-ORDER RATE CONSTANTS FOR Cl^- ANATION OF $Ir(OH_2)_2Cl_4^-$

Run no.	Temp., °C.	C_0, mF	μ,[a] F	(H^+),[b] F	(Cl^-), F	10^5k_{-2}, M^{-1} sec.$^{-1}$[c]
16	50.00	3.63	2.22	1.02	1.00	6.31 ± 0.51[d] 8.61 ± 0.13[e]
15	50.00	3.64	2.22	1.02	1.00	6.56 ± 0.21[d] 8.73 ± 0.09[e]
13	50.00	4.33	2.22	1.02	1.00	6.39 ± 0.13[d] 6.78 ± 0.23[e]
14	50.00	4.53	2.22	1.02	1.00	6.82 ± 0.14[d] 7.52 ± 0.17[e]
17	50.00	4.08	2.22	1.02	0.30	6.27 ± 0.07[d] 5.67 ± 0.11[e]
23	50.00	4.25	3.54	1.02	0.30	5.60 ± 0.27[d] 6.38 ± 0.83[e]
21	50.00	4.06	3.70	1.02	0.30	5.63 ± 0.16[d] 6.53 ± 0.15[e]
20	50.00	4.13	3.70	2.50	0.30	6.50 ± 0.33[d] 7.87 ± 0.40[e]
19	50.00	4.17	3.70	2.50	0.60	6.40 ± 0.23[d] 6.85 ± 0.38[e]
18	50.00	4.19	3.70	2.50	0.90	6.43 ± 0.49[d] 7.13 ± 0.69[e]
22	50.00	4.06	3.72	0.15	0.30	5.33 ± 0.20[d] 5.64 ± 0.50[e]
24	40.00	4.14	3.70	2.50	0.90	1.69 ± 0.05[d] 2.13 ± 0.05[e]
25	24.95	4.20	3.70	2.50	0.90	0.167 ± 0.003[d] 0.197 ± 0.009[e]

[a] Ionic strength adjusted with $NaCl + NaClO_4$. [b] 0.15 F HNO_3, rest from $HClO_4$. [c] Obtained from a least-squares analysis; errors given are statistical standard deviations, and actual errors probably are 10–20%. [d] Spectrophotometrically, 485 mμ. [e] Spectrophotometrically, 500 mμ.

spectrum of the Ir(III) reactant and products unless these are oxidized to Ir(IV). Because of this effect the errors in the rate constants are much larger than in the aquation studies, being perhaps 10–20%. The rate data were analyzed with the first-order rate equation

$$\ln [(A_0 - A_\infty)/(A - A_\infty)] = k'_{-2}t \qquad (4)$$

where A_0 and A are the optical absorbancies, measured at a given wave length, of oxidized aliquots of the reaction solution at reaction times zero and t, respectively, A_∞ is the absorbancy calculated on the assumption all complex has been anated to $Ir(OH_2)Cl_5^{-2}$ and then oxidized to $Ir(OH_2)Cl_5^-$, and k'_{-2} is the pseudo-first-order rate constant for the anation of $Ir(OH_2)_2Cl_4^-$ (reverse reaction 2) at a given constant concentration of Cl^-. The second-order rate constant k_{-2} was taken as $k'_{-2}/(Cl^-)$, where (Cl^-) was set equal to the formal concentration of Cl^-. The results are presented in Table III.

Good first-order plots were obtained over 10–20% anation. Over this same reaction extent the spectra of oxidized aliquots of reaction solution exhibited two good isosbestic points at 519–523 mμ (a_M = 1280 ± 20 M^{-1} cm.$^{-1}$) and 391–394 mμ (a_M = 965 ± 20 M^{-1} cm.$^{-1}$), *vs.* 520 mμ (a_M = 1260 M^{-1} cm.$^{-1}$) and 395 mμ (a_M = 980 M^{-1} cm.$^{-1}$) expected theoretically from Figure 2 for the $Ir(OH_2)_2Cl_4^-$–$Ir(OH_2)Cl_5^{-2}$ system after Cl_2 oxidation to the $Ir(OH_2)_2Cl_4$–$Ir(OH_2)Cl_5^-$ system. The first of these two theoretical isosbestic points also coincides with an isosbestic point for the $Ir(OH_2)Cl_5^-$–$IrCl_6^{-2}$ system (518 mμ, a_M = 1280 M^{-1} cm.$^{-1}$) and is present nearly unchanged beyond 20% anation of $Ir(OH_2)_2Cl_4^-$. Of the remaining three isosbestic points expected from Figure 2, only the one at 615 mμ was noted (at *ca.* 600–630 mμ, absorbancies being too low to allow a more accurate identification); the ones at 359 and 353 mμ were obscured by interference from the spectrum of Cl_2 present in the oxidized aliquots.

Values of k_{-2} found at 485 and 500 mμ for a given set of reaction conditions did not always agree within the apparent experimental error, probably because of small errors in the calculated values of A_∞ and the interference from $IrCl_6^{-2}$ formed. Errors for the 500-mμ values are estimated to be twice those for the 485-mμ values, and weighted averages of k_{-2} were calculated accordingly.

At 50.00° and 2.50 F H^+ (μ = 3.70) the anation rate law is $-d(Ir(OH_2)_2Cl_4^-)/dt = k_{-2}(Cl^-)(Ir(OH_2)_2Cl_4^-)$ over the range 0.3–0.9 F Cl^- (runs 18–20), with k_{-2} = (6.7 ± 0.4) × 10^{-5} M^{-1} sec.$^{-1}$. This rate constant is *ca.* one-half that found[2] for Cl^- anation of $Ir(OH_2)Cl_5^{-2}$ at 50° at essentially the same H^+ concentration and ionic strength. At 1.02 F H^+ and 0.30 F Cl^-, k_{-2} is independent of the ionic strength over the range 2.22–3.70 within the experimental error (runs 17, 23, 21). Runs 20–22 at 0.3 F Cl^- (μ = 3.70–3.72) show a 22 ± 2% decrease in k_{-2} over the 17-fold decrease in H^+ concentration from 2.5 to 0.15 F. A similar effect was observed[2] in the Cl^- anation of $Ir(OH_2)Cl_5^{-2}$. Since the effect is not much greater than the experimental errors, an attempt to deduce the form of a (H^+)-dependent term in the rate law is unwarranted. The effect cannot be due to acid properties of $Ir(OH_2)_2Cl_4^-$, inasmuch as our potentiometric titrations of *ca.* 10 mF $Ir(OH_2)_2Cl_4^-$ (0.3 F HNO_3 effluent, first neutralized with 0.3 F NaOH) with 0.01 F NaOH gave pK_a values of 8.46 ± 0.42 and 10.1 ± 0.5 at *ca.* 25° for the first and second acid dissociations, respectively, ruling out the presence of appreciable hydroxo complexes.

The Arrhenius activation energy E_a for the Cl^- anation of $Ir(OH_2)_2Cl_4^-$ was obtained from a linear plot of log k_{-2} *vs.* $1/T$ (runs 18, 24, 25); E_a = 27.8 ± 0.6 kcal. and log pZ = 14.6 ± 0.4 (M^{-1} sec.$^{-1}$).

Aquation–Anation Equilibrium Quotient.—Values of the concentration equilibrium quotient K for reaction 2, obtained from the ratio of the aquation–anation rate constants (k_2/k_{-2}), are given in Table IV. Within experimental error, K is constant over the range 1.02–2.55 F H^+ (μ = 3.70–3.75) at 50.00°. Although K increases with decreasing ionic strength, the data are not sufficiently accurate and the ionic strengths are too high to justify an extrapolation to infinite dilution. At 40–50° $\Delta H°$ for the anation reaction appears to be small.

Rate of Aquation of $Ir(OH_2)_2Cl_4^-$.—A single preliminary experiment was made on the rate of the aquation reaction

$$Ir(OH_2)_2Cl_4^- + H_2O \xrightarrow{k_3} Ir(OH_2)_3Cl_3 + Cl^- \qquad (5)$$

TABLE IV

t, °C.	(H^+), F	μ, F	10^5k_2, sec.$^{-1}$	10^5k_{-2}, M^{-1} sec.$^{-1}$	K, M
40.00	2.50–2.55	3.70–3.75	0.397 ± 0.021	1.83 ± 0.05	0.215 ± 0.017
50.00	2.50–2.55	3.70–3.75	1.34 ± 0.07	6.07 ± 0.08	0.221 ± 0.014
50.00	1.02	3.70–3.75	1.24 ± 0.02	5.93 ± 0.16	0.209 ± 0.009
50.00	1.02	2.22	1.84 ± 0.05	6.53 ± 0.15	0.280 ± 0.014

in 2.5 F $HClO_4$–1.2 F $NaClO_4$ at 50.00° in the dark, primarily to see if this reaction needed to be taken into consideration in our analysis of the rate data on $Ir(OH_2)Cl_5^{-2}$ aquation and if any information on the possible *cis–trans* isomerization of the diaquo species could be obtained by this means.

Absorption spectra taken of Cl_2-oxidized aliquots of the reaction solution at times up to 40% reaction exhibited isosbestic points at 535 mμ (a_M = 1330 M^{-1} cm.$^{-1}$), 488 mμ (a_M = 1260 M^{-1} cm.$^{-1}$), and 402 mμ (a_M = 993 M^{-1} cm.$^{-1}$), *vs.* 529 mμ (a_M = 1300 M^{-1} cm.$^{-1}$), 489 mμ (a_M = 1290 M^{-1} cm.$^{-1}$), and 404 mμ (a_M = 1070 M^{-1} cm.$^{-1}$) expected theoretically for the $Ir(OH_2)_2Cl_4$–$Ir(OH_2)_3Cl_3^+$ system (see Figure 2). The agreement is satisfactory, considering the errors introduced from the Cl_2 absorption (which is difficult to balance out exactly in the reference cell). Hence, the reaction is aquation and the aquation product is the expected $Ir(OH_2)_3Cl_3$.

The aquation rate was followed by titration of released Cl^- and by spectrophotometric measurements on Cl_2-oxidized aliquots of reaction solution at 440 and 460 mμ, where differences in the molar absorbancy indices of $Ir(OH_2)_2Cl_4$ and $Ir(OH_2)_3Cl_3^+$ are the largest; A_∞ was calculated from the known spectrum of $Ir(OH_2)_3Cl_3^+$ (Figure 2). The rate constants, presented in Table V, were evaluated from first-order rate plots which were linear over the first 10% reaction for Cl^- release and 25% reaction for the spectrophotometric method; beyond these reaction extents the plots exhibited a slight curvature in the direction corresponding to a back reaction.

TABLE V

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF $Ir(OH_2)_2Cl_4^-$ IN 2.5 F $HClO_4$–1.2 F $NaClO_4$ AT 50.00°

(C_0 = 3.6 mF)

Method	10^5k_3, sec.$^{-1}$
Cl^- release	0.30 ± 0.01
Spectrophotometric, 440 mμ	0.27 ± 0.01
Spectrophotometric, 460 mμ	0.30 ± 0.01
	Av. 0.29 ± 0.01 ($t_{1/2}$ = 67 hr.)

At 50° in 2.5 F H^+ (μ = 3.7) aquation of $Ir(OH_2)Cl_4^-$ is 4.4-fold slower than aquation of $Ir(OH_2)Cl_5^{-2}$, and the former aquation does not significantly effect our methods of calculating rate constants for the latter aquation. A detailed study of reaction 5 and its back reaction is planned for the future.

Discussion

Spectra.—Figure 1 shows that the absorption spectra of the Ir(III) complexes $IrCl_6^{-3}$, $Ir(OH_2)Cl_5^{-2}$, $Ir(OH_2)_2Cl_4^-$, and $Ir(OH_2)_3Cl_3$ are all similar except for displacement toward shorter wave lengths and increase in relative intensity of the shorter wave-length band as the number of ligand water molecules per Ir increases; the former effect is expected from the relative positions of H_2O and Cl^- in the spectrochemical series. Figure 2 shows that the spectral differences among the corresponding Ir(IV) complexes are much greater. According to Jørgensen,[13,14] these spectra of $IrCl_6^{-2}$ and $Ir(OH_2)Cl_5^-$ are charge-transfer spectra. Assuming likewise for the other two Ir(IV) complexes, we would not expect the Ir(IV) spectra to exhibit the correlation noted for the Ir(III) complexes. Orgel[15] has pointed out that in cases where charge-transfer bands are toward the red end of the visible spectrum, obscuring the weaker d–d bands (as seen in Figure 2), easy reducibility of the central metal atom of the complex by a slightly more oxidizable ligand is to be expected; the spectra of $Ir(OH_2)_3Cl_3^+$ and $Ir(OH_2)_2Cl_4$ are thus in accord with our finding that these species are readily reduced on the anion-exchange resin columns used to effect their separation.

Aquation and Isomerization Reactions.—Neither chromatographic nor kinetic evidence exists for more than one of the two theoretically possible geometrical isomers of the diaquo and triaquo species in any of the solutions involved in this study. The kinetic results require that $Ir(OH_2)_2Cl_4^-$ (and probably $Ir(OH_2)_3Cl_3$) isomerizes at 50° in the acid media involved with $t_{1/2}$ $\ll$15 hr. *or* $\gg$67 hr. (intermediate values conflict with the observed existence of isosbestic points in both $Ir(OH_2)Cl_5^{-2}$ and $Ir(OH_2)_2Cl_4^-$ aquation and with the essential equality of k_2 values found spectrophotometrically, by Cl^- release, and from unreacted reactant). In either case, k_2 and k_3 are accurate measures of aquation rates. If $t_{1/2}$ $\ll$ 15 hr., either $Ir(OH_2)_2Cl_4^-$ or $Ir(OH_2)_3Cl_3$, or both, would always be present in our solutions as an equilibrium mixture of the two isomers. However, probably only one isomer of $Ir(OH_2)_2Cl_4^-$ ($t_{1/2}$ $\gg$ 67 hr.) was ever present here, since the *same* isosbestic points were found in $Ir(OH_2)Cl_5^{-2}$ aquation at 65° as at 50°, whereas the *cis–trans* ratio probably would be significantly different at 65 and 50°.

At 50° in 2.5 F $HClO_4$–1.2 F $NaClO_4$ the aquation rate constants for $IrCl_6^{-3}$, $Ir(OH_2)Cl_5^{-2}$, and $Ir(OH_2)_2Cl_4^-$ are in the ratio of *ca.* 1500 (ref. 2):100:22.[16] Since the crystal-field splitting is larger for H_2O than for Cl^-, the crystal-field contribution to the activation energy should increase for substitution reactions of the

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[13] C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 518 (1956).

[14] C. K. Jørgensen, *Mol. Phys.*, **2**, 309 (1959).

[15] L. E. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand-Field Theory," John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 100, 101.

[16] Using a rough method, Poulsen and Garner[2] showed that $k_2 \lesssim 0.1k_1$ at 50 and 25°, an upper limit in accord with our more accurate values of k_2.

above complexes in the order given. Actually, the activation energies are the same within the experimental errors in aquation of $IrCl_6^{-3}$ ($E_a = 30.4 \pm 2.0$ kcal., log $pZ = 17.5 \pm 1.8$ (sec.$^{-1}$)[2]) and $Ir(OH_2)Cl_5^{-2}$ ($E_a = 29.4 \pm 0.6$ kcal., log $pZ = 15.1 \pm 0.4$ (sec.$^{-1}$)); presumably other factors are contributing significantly to the activation energies.

Apparently little research on aquation kinetics of other 5d MX^n and $M(OH_2)X^m$ complexes has been published. Martinez[17] studied the aquation of $IrCl_6^{-2}$ and its exchange with Cl^{*-}, but the results may have been affected by a possible catalytic path involving traces of $IrCl_6^{-3}$ formed in the reaction solutions[18]; her value of 1.01×10^{-6} sec.$^{-1}$ for the aquation rate constant at 50° may be only an upper limit, with $E_a = 20.2 \pm 0.9$ kcal. as a lower limit. The kinetics of aquation of $OsCl_6^{-2}$ in HNO_3 and in HCl media has been investigated[19]; in 0.00001–0.1 F H^+ ($\mu = 0.5$–1.32) at 79.53° the aquation rate constant is 3.5×10^{-6} sec.$^{-1}$, $E_a = 33.1 \pm 0.6$ kcal., and log $pZ = 15.1 \pm 0.4$ (sec.$^{-1}$). Thus, at 50° the aquation rate constants for $Ir(OH_2)Cl_5^{-2}$, $OsCl_6^{-2}$, and $IrCl_6^{-2}$ are in the ratio of *ca.* 1000:4:80; activation energies increase in the order d^5 $IrCl_6^{-2}$(?), d^6 $Ir(OH_2)Cl_5^{-2}$, d^4 $OsCl_6^{-2}$. Hydrolysis rates of $PtCl_6^{-2}$ and $PtBr_6^{-2}$ have been measured,[20,21] but meaningful rates and rate laws have not been established.

Additional kinetic studies on 5d complexes are desirable, both as an extension of our knowledge of transition metal complexes and to allow isolation of the important factors governing the rates of substitution reactions of such complexes.

[17] M. R. Martinez, "Aquation and Radiochloride Exchange of Hexachloroiridate(IV) Ion," Ph.D. Dissertation, U.C.L.A., June 1958.

[18] The same catalytic path presumably would affect the interpretations made by E. Blasius, W. Preetz, and R. Schmitt, *J. Inorg. Nucl. Chem.*, **19**, 115 (1961), in their study of $IrCl_6^{*-2}$–Cl^- exchange rates. They also studied the $IrCl_6^{*-3}$–Cl^- exchange, but reported no rate law or rate constants and did not state the temperature of the system.

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[20] E. H. Archibald, *J. Chem. Soc.*, 1104 (1920).

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Raman Spectroscopic and E.m.f. Studies on Aqueous Solutions of the *trans*-Tetrahydroxidodimethylstannate(IV) Ion. The Four Acid Dissociation Constants of the Dimethyltin(IV) Aquo Ion[1]

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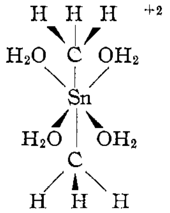
The proton-transfer equilibria of the dimethyltin(IV) ion have been studied in alkaline solutions at 25° by e.m.f. measurements. These data combined with those from earlier studies on acidic solutions give the following values for the four stepwise acid dissociation constants for the dimethyltin(IV) aquo ion in a medium with $[Cl^-] = 0.1$ M: $\log K_1 = -3.25 \pm 0.01$, $\log K_2 = -5.27 \pm 0.02$, $\log K_3 = -11.5 \pm 0.1$, $\log K_4 = -11.7 \pm 0.1$. The Raman spectra of strongly alkaline solutions of the dimethyltin(IV) ion have been assigned on the basis of a *trans* octahedral structure for the tetrahydroxidodimethylstannate(IV) anion. Proton n.m.r. studies indicate that the tetrahydroxidodimethylstannate(IV) ion decomposes slowly in strong base giving primarily the hexahydroxostannate(IV) and a trimethyltin(IV) species. The solution behavior of the aquodimethyltin(IV) ion and the low Raman intensity of the tin–oxygen bond stretching vibrations indicate that this ion is very similar in its behavior to other simple multivalent cations. The assignment of tin–oxygen stretching frequencies in organotin compounds is also discussed.

Introduction

In 1953, Rochow and Seyferth studied the hydrolysis of dimethyltin dichloride and also observed that freshly precipitated dimethyltin oxide dissolved when about 2 moles of sodium hydroxide per mole of oxide had been added.[2] This led them to suggest the formation of $Na_2[(CH_3)_2Sn(OH)_4]$ as the soluble species in the alkaline solutions.

Recent Raman, infrared, and n.m.r. spectroscopic studies[3] have shown that aqueous solutions of dimethyltin(IV) compounds contain an aquo ion with a linear C–Sn–C skeleton, and the vibrational spectra were assigned on the basis of effective D_{3d} symmetry. In all probability the cation contains four water molecules in the first coordination sphere bound essentially by ion–dipole forces and has the structure I. By comparison with I, it would be expected that a tetrahydroxidodimethylstannate(IV) could be formed in strongly alkaline solutions by removal of one proton from each of the coordinated water molecules in the aquo ion.



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