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Kinetics of Aquation of *cis*- and *trans*-Diaquotetrachloroiridate(III) Anions and Chloride Anation of 1,2,6-Triaquotrichloroiridium(III)[1]

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The kinetics of the reaction *trans*-$\mathrm{Ir(OH_2)_2Cl_4^-} + \mathrm{H_2O} \xrightarrow{k_{3T}}$ 1,2,6-$\mathrm{Ir(OH_2)_3Cl_3} + \mathrm{Cl^-}$ was studied in perchlorate and mixed nitrate–perchlorate media at 50–80° spectrophotometrically and by titration of released chloride. In 2.5 F $\mathrm{HClO_4}$–1.2 F $\mathrm{NaClO_4}$ at 50.00° $k_{3T} = (5.1 \pm 0.2) \times 10^{-7}$ sec^{-1}, independent of (*trans*-$\mathrm{Ir(OH_2)_2Cl_4^-}$)$_0$ from 0.5 to 1 mF. $E_a = 30.5 \pm 0.9$ kcal and $\log pZ = 14.3 \pm 0.4$; $k_{3T} \sim 8 \times 10^{-9}$ sec^{-1} at 25° by extrapolation. At 80.00° k_{3T} is essentially independent of (*trans*-$\mathrm{Ir(OH_2)_2Cl_4^-}$)$_0$ from 0.2 to 5 mF and of ($\mathrm{H^+}$) from 1.0 to 2.5 F ($\mu = 3.8$–4.0, $\mathrm{NaClO_4}$). In mixed nitrate–perchlorate medium at 50–80° the rate law was found to be $-\mathrm{d}(trans\text{-}\mathrm{Ir(OH_2)_2Cl_4^-})/\mathrm{d}t = [k_{3T} + k_{3TN}(\mathrm{NO_3^-})](trans\text{-}\mathrm{Ir(OH_2)_2Cl_4^-})$, where ($\mathrm{NO_3^-}$) is taken as the $\mathrm{NO_3^-}$ formality (0.0–1.1). In 2.5 F $\mathrm{HClO_4}$–1.2 F $\mathrm{NaClO_4}$ at 50.00° k_{3T} obtained by extrapolation to ($\mathrm{NO_3^-}$) = 0 was the same as in perchlorate medium within experimental error; $k_{3TN} = (9.1 \pm 0.3) \times 10^{-6}$ M^{-1} sec^{-1}, independent of (*trans*-$\mathrm{Ir(OH_2)_2Cl_4^-}$)$_0$ from 0.7 to 5 mF. $E_a = 24.0 \pm 0.6$ kcal and $\log pZ = 11.1 \pm 0.3$ for the $\mathrm{NO_3^-}$ path; by extrapolation, $k_{3TN} \sim 4 \times 10^{-7}$ M^{-1} sec^{-1} at 25°. At 80.00° k_{3TN} was essentially constant from 0.4 to 5 mF (*trans*-$\mathrm{Ir(OH_2)_2Cl_4^-}$)$_0$ and from 1.0 to 3.2 F ($\mathrm{H^+}$) at $\mu = 3.6$–4.2. Chloride anation of 1,2,6-$\mathrm{Ir(OH_2)_3Cl_3}$ was studied at 50–60° in 2.4 F $\mathrm{HClO_4}$ ($\mu = 3.7$, $\mathrm{NaClO_4} + \mathrm{NaCl}$). A rate law $-\mathrm{d}(1,2,6\text{-}\mathrm{Ir(OH_2)_3Cl_3})/\mathrm{d}t = k_{-3T}(1,2,6\text{-}\mathrm{Ir(OH_2)_3Cl_3})(\mathrm{Cl^-})$ was found, where ($\mathrm{Cl^-}$) is taken as the $\mathrm{Cl^-}$ formality (0.3–1.0). At 50.00° $k_{-3T} = (2.2 \pm 0.2) \times 10^{-5}$ M^{-1} sec^{-1}. $E_a = 28.8 \pm 0.6$ kcal and $\log pZ = 14.7 \pm 0.3$; $k_{-3T} \sim 5 \times 10^{-7}$ M^{-1} sec^{-1} at 25° by extrapolation. At 80.00° *cis*-$\mathrm{Ir(OH_2)_2Cl_4^-}$ aquates in 2.4 F $\mathrm{HClO_4}$–1.2 F $\mathrm{NaClO_4}$–0.3 F $\mathrm{NaHSO_4}$ with a first-order rate law, with $k_{3C} = (2.56 \pm 0.07) \times 10^{-5}$ sec^{-1}, essentially the same rate constant as for *trans*-$\mathrm{Ir(OH_2)_2Cl_4^-}$ aquation. The products are *ca.* 60% 1,2,3-$\mathrm{Ir(OH_2)_3Cl_3}$ and 40% 1,2,6-$\mathrm{Ir(OH_2)_3Cl_3}$. Mechanisms are discussed, and evidence is presented for nitrate complexing of iridium(III). The previously unreported species, *cis*- and *trans*-$\mathrm{Ir(OH_2)_2Cl_4^-}$, *cis*- and *trans*-$\mathrm{Ir(OH_2)_2Cl_4}$, 1,2,3- and 1,2,6-$\mathrm{Ir(OH_2)_3Cl_3}$, and 1,2,3- and 1,2,6-$\mathrm{Ir(OH_2)_3Cl_3^+}$, were isolated in solution and their visible absorption spectra obtained. At 25° for 1,2,3-$\mathrm{Ir(OH_2)_3Cl_3}$ = 1,2,3-$\mathrm{Ir(OH_2)_3Cl_3^+} + \mathrm{e^-}$, $E° = -1.30 \pm 0.01$ v in 0.4 F $\mathrm{HClO_4}$ or $\mathrm{HNO_3}$, and for *trans*-$\mathrm{Ir(OH_2)_2Cl_4^-}$ = *trans*-$\mathrm{Ir(OH_2)_2Cl_4} + \mathrm{e^-}$, $E° = -1.22 \pm 0.02$ v in 0.4 F $\mathrm{HClO_4}$–0.2 F $\mathrm{NaH_2PO_4}$, *vs.* standard $\mathrm{H_2}$–$\mathrm{H^+}$ couple; these Ir(IV) complexes are strong oxidants.

Introduction

In extension of a study[2] of the aquation of hexachloroiridate(III) anion and chloride anation[3] of aquopentachloroiridate(III) anion and a study[4] of the

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

aquation of aquopentachloroiridate(III) anion and chloride anation of *trans*-diaquotetrachloroiridate(III) anion,[5] we report here an investigation of the kinetics

$$\mathrm{Ir(OH_2)Cl_5^{2-}} + \mathrm{H_2O} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} trans\text{-}\mathrm{Ir(OH_2)_2Cl_4^-} + \mathrm{Cl^-} \tag{2}$$

of aquation of *cis*- and *trans*-diaquotetrachloroiridate(III) anions and chloride anation of 1,2,6-triaquotrichloroiridium(III)[6]

$$trans\text{-}\mathrm{Ir(OH_2)_2Cl_4^-} + \mathrm{H_2O} \xrightarrow{k_{3T}} 1,2,6\text{-}\mathrm{Ir(OH_2)_3Cl_3} + \mathrm{Cl^-} \tag{3}$$

$$cis\text{-}\mathrm{Ir(OH_2)_2Cl_4^-} + \mathrm{H_2O} \xrightarrow{k_{3C}} \mathrm{Ir(OH_2)_3Cl_3}\text{ isomers} + \mathrm{Cl^-} \tag{4}$$

$$1,2,6\text{-}\mathrm{Ir(OH_2)_3Cl_3} + \mathrm{Cl^-} \xrightarrow{k_{-3T}} \mathrm{Ir(OH_2)_2Cl_4^-}\text{ isomers} + \mathrm{H_2O} \tag{5}$$

together with qualitative observations on the aquation of the triaquo complexes.

In the presence of nitrate ion, *trans*-diaquotetrachloroiridate(III) anion disappears faster than in the absence of nitrate ion at the same temperature, and we have investigated the kinetics of the reactions involved. Evidence is presented for formation of a nitrate complex of iridium(III).

The species reported earlier[4] as diaquotetrachloroiridate(III) anion, diaquotetrachloroiridium(IV), triaquotrichloroiridium(III), and triaquotrichloroiridium(IV) cation of unknown geometric configuration have now been characterized as the *trans*-diaquo and 1,2,6-triaquo isomers. We report also the isolation in solution of the *cis*-diaquo and 1,2,3-triaquo isomers and the visible absorption spectra of these new complexes. Oxidation potentials have been determined for the *trans*-diaquo and 1,2,3-triaquo complexes.

Experimental Section

Ammonium Aquopentachloroiridate(III).—This compound was prepared as described earlier,[4] using commercial $\mathrm{(NH_4)_2IrCl_6}$ (Fairmount Chemical Co., Inc., Newark, N. J.) analyzed by Pacific Spectrochemical Laboratory, Los Angeles, Calif., and found to contain 0.01% Rh and no other Pt metals.

Anal. Calcd for $\mathrm{(NH_4)_2[Ir(OH_2)Cl_5]}$: Ir, 45.37; Cl, 41.85. Found: Ir, 45.37; Cl, 40.67.

The visible absorption spectra in 2.5 F $\mathrm{HClO_4}$–1.2 F $\mathrm{NaClO_4}$, before and after oxidation with $\mathrm{Cl_2}$, checked well with those reported by Chang and Garner.[4]

Chromatography of Boiled Aquopentachloroiridate(III) Solution.—The Ir(III) species described in this paper were obtained

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(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) J. C. Chang and C. S. Garner, *Inorg. Chem.*, **4**, 209 (1965).

(5) Assignment of the $\mathrm{Ir(OH_2)_2Cl_4^-}$ species involved as the *trans* isomer is reported in the present paper.

(6) In this complex two of the water ligands are *trans* to each other and *cis* to the third water ligand. In the 1,2,3-triaquo isomer, referred to later, all three water ligands are *cis* to one another.

by anion-exchange chromatography of $(NH_4)_2[Ir(OH_2)Cl_5]$–$HClO_4$ solutions which were boiled (*caution*[7]) and then treated with Cl_2 (*caution*[7]), and the Ir(IV) species were adsorbed on a 1-cm diameter × 25-cm column of HSO_4^- Dowex AG 1X-8 (100–200 mesh) resin.[8,9] With 0.3–0.5-g amounts of $(NH_4)_2[Ir(OH_2)Cl_5]$, the Ir species adsorbed on the top 5–7 cm of the column.

Although it was possible to obtain reasonably pure fractions of 1,2,6- and 1,2,3-$Ir(OH_2)_3Cl_3$ and *trans*- and *cis*-$Ir(OH_2)_2Cl_4^-$ by successive elution off a resin column, solutions of the individual complexes were prepared more satisfactorily by the procedures below.

1,2,6-Triaquotrichloroiridium(III).—One-half gram of $(NH_4)_2[Ir(OH_2)Cl_5]$ was dissolved in 10 ml of 1 *F* $HClO_4$, boiled for 2 min (*caution*[7]), and cooled; Cl_2 was passed in for 15 min (*caution*[7]), and then the solution was poured onto a HSO_4^- resin column (*vide ante*). Elution of 1,2,6-$Ir(OH_2)_3Cl_3$ was carried out with 0.01 *F* $HClO_4$, discarding the first 10 ml and collecting the next 25 ml. This greenish yellow effluent was 3 m*F* in the desired complex. A Cl:Ir atom ratio of 3.01 was found. No cationic Ir species were found.

1,2,6-Triaquotrichloroiridium(IV) Cation.—This complex was obtained by oxidation of the Ir(III) complex in 0.1-saturated Cl_2–2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$, giving an orange-red solution.

1,2,3-Triaquotrichloroiridium(III).—A solution of 0.3 g of $(NH_4)_2[Ir(OH_2)Cl_5]$ in 10 ml of 0.05 *F* $HClO_4$ was boiled 10 min (*caution*[7]) and cooled; Cl_2 was passed in for 15 min (*caution*[7]); then the solution was poured onto a HSO_4^- resin column (*vide ante*). Elution with 0.02 *F* $HClO_4$ was performed, discarding the first 20 ml (containing 1,2,6-$Ir(OH_2)_3Cl_3$ and some 1,2,3 isomer) and collecting the next 80 ml. The latter greenish yellow solution of 1,2,3-$Ir(OH_2)_3Cl_3$ was 1 m*F* and was free from cationic Ir species; it had a Cl:Ir atom ratio of 3.00.

1,2,3-Triaquotrichloroiridium(IV) Cation.—Oxidation of the corresponding Ir(III) complex in 0.1-saturated Cl_2–2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$ gave the Ir(IV) complex as a violet-red solution.

***trans*-Diaquotetrachloroiridate(III) Anion.**—A solution of 0.3 g of $(NH_4)_2[Ir(OH_2)Cl_5]$ in 10 ml of 1 *F* $HClO_4$ was boiled 10 min (*caution*[7]) and cooled; Cl_2 was passed in for 15 min (*caution*[7]); then the solution was poured onto a HSO_4^- resin column (*vide ante*). Triaquo species were eluted with 150 ml of 0.01 *F* $HClO_4$ and discarded. Elution with 0.6 *F* $NaHSO_4$ was used to obtain *trans*-$Ir(OH_2)_2Cl_4^-$, discarding the first 30 ml of effluent and collecting the next 70 ml. The latter greenish yellow solution was 5 m*F* in the *trans* complex and gave a Cl:Ir ratio of 4.03 and 1.07 reduction equiv/g-atom of Ir. When the diaquo complex was needed free from HSO_4^-, it was obtained (after first eluting the triaquo species with 100 ml of 0.001 *F* $HClO_4$) by elution off a NO_3^- Dowex AG 1-X8 column with 1 *F* NaH_2PO_4, discarding the first 30 ml and collecting the next 150 ml, which was *ca.* 1 m*F* in *trans*-$Ir(OH_2)_2Cl_4^-$. Occasionally, elution with 0.6 *F* $NaHSO_4$ from an NO_3^- resin column was used, discarding the first 40 ml and collecting the next 100 ml.

***trans*-Diaquotetrachloroiridium(IV).**—This neutral complex was made by Cl_2 oxidation of a *trans*-$Ir(OH_2)_2Cl_4^-$ solution, giving a brownish red solution.

***cis*-Diaquotetrachloroiridate(III) Anion.**—After elution of *trans*-$Ir(OH_2)_2Cl_4^-$ (*vide ante*), elution with 0.6 *F* $NaHSO_4$ was continued. The next *ca.* 130 ml of effluent was colorless and was discarded, as was the next 10 ml, which was colored. Then the next 100 ml was collected, giving a 1 m*F* greenish yellow solution of *cis*-$Ir(OH_2)_2Cl_4^-$, with a Cl:Ir atom ratio of 4.06.

***cis*-Diaquotetrachloroiridium(IV).**—This neutral complex was obtained by oxidation of the Ir(III) complex with Cl_2, giving a yellow-brown solution. This complex and the other Ir(IV) complexes are easily reduced to the Ir(III) state with H_2O_2.

Sodium Perchlorate.—Reagent grade Na_2CO_3 was neutralized with reagent grade $HClO_4$. The resulting solution was evaporated on a steam bath to crystallization. The $NaClO_4$ obtained was recrystallized twice from distilled water.

Other Chemicals.—All other chemicals were 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.—Solid Ir compounds were analyzed for Ir and Cl as described previously,[4] as was ligand Cl in solution, and the number of reduction equivalents ($KMnO_4$ titration only). Iridium in solution was also determined as described earlier,[4] except that 0.1-saturated Cl_2 solution was used in place of the saturated Cl_2 solution.

Oxidation Potentials.—Approximate values of the standard oxidation potential $E°$ for the reversible couples 1,2,3-$Ir(OH_2)_3Cl_3$ = 1,2,3-$Ir(OH_2)_3Cl_3^+ + e^-$ (in 0.4 *F* $HClO_4$ or HNO_3) and *trans*-$Ir(OH_2)_2Cl_4^-$ = *trans*-$Ir(OH_2)_2Cl_4 + e^-$ (in 0.4 *F* $HClO_4$–0.2 *F* NaH_2PO_4) were determined at 25° by the method given earlier.[4] Oxidation of 1,2,3-$Ir(OH_2)_3Cl_3$ and *trans*-$Ir(OH_2)_2Cl_4^-$ by $KMnO_4$ was slow, and after each addition of $KMnO_4$ 5 min was allowed before reading the emf. Ignoring presumably small liquid-junction potentials, we obtain $E° = -1.30 \pm 0.01$ and -1.22 ± 0.02 v, respectively.[10] The latter value agrees with that found by Chang and Garner[4] for the diaquo couple in 0.4 *F* HNO_3.

Kinetic Runs.—Reaction solutions were prepared from chromatographed *cis*- or *trans*-$Ir(OH_2)_2Cl_4^-$ or 1,2,3- or 1,2,6-$Ir(OH_2)_3Cl_3$ and O_2-free stock solvents of $HClO_4$ and $NaClO_4$. Known weights of $NaNO_3$ or known volumes of standard HNO_3 were added for NO_3^--dependence experiments. In chloride-anation runs known weights of NaCl were added.

Reaction solutions were further deaerated with an N_2 stream, and then 5–7-ml portions were sealed by torch in Pyrex ampoules flushed out with N_2. To exclude light each ampoule was wrapped in Al foil. Ampoules were placed in baths thermostated at 50.00 ± 0.02, 65.00 ± 0.02, and 80.00 ± 0.02° (aquation runs) or 50.00 ± 0.02 and 60.00 ± 0.02° (anation runs). For 80° runs, ampoules were heated to *ca.* 80° by immersion in a 100° bath for 45 sec and then transferred at once to the 80° thermostated bath; zero reaction time was taken as 3 min later. For the other runs, zero reaction time was taken as 10 min after the ampoules were placed directly in the baths. Ampoules were removed at known times, quenched in ice, and then refrigerated at 10° until they could be analyzed (within 1 day) by the methods described below.

Spectrophotometry.—Aliquots (1.00, 2.00, or occasionally 10.00 ml) of reaction solution were diluted to 50.00 ml with a 0.1-saturated Cl_2 solution[11] which was 2.5 *F* in $HClO_4$ and 1.2 *F* in $NaClO_4$, and the optical absorbancy was measured 10–20 min later (aquation runs) and 2 hr later (anation runs) at *ca.* 25° in matched 10.00-cm silica cells with a Beckman DU spectrophotometer at 440 and 460 mμ (aquation runs) and at 420, 440, and 460 mμ (anation runs).

The visible absorption spectra of separated Ir(III) complexes were obtained in O_2-free 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$ at *ca.* 25° in matched 1.00- or 10.00-cm silica cells with a Cary Model 11 recording spectrophotometer within 5 min after preparation of the solutions. Spectra of the Ir(IV) complexes were determined likewise, except for dilution of 1 ml with 50 ml of 0.1-saturated

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[7] A safety shield should be used. Although explosions were not experienced under the conditions used, NH_4ClO_4 can be exploded under appropriate conditions, and explosive NCl_3 can form from NH_4^+ salts and Cl_2.

[8] Cl_2 is used to oxidize Ir(III) to Ir(IV), in which state the monoaquo and diaquo complexes adsorb readily on the resin (see ref 2 and 4). All iridium species eluted are, however, 100% in the Ir(III) state. Even the neutral Ir species are adsorbed on the resin, but are very easily eluted.

[9] Conversion of commercially available Cl^- Dowex AG 1X-8 resin to the HSO_4^- form was achieved by washing with 1 *F* $NaHSO_4$ until the washings gave a negative test for Cl^- with $AgNO_3$. Excess $NaHSO_4$ was removed by washing with water; then resin columns were prepared and prefilled with 0.01 *F* $HClO_4$.

[10] As used here, a negative value of $E°$ means that the reduced form of the couple is thermodynamically a weaker reducing agent than H_2 in the standard H_2–H^+ couple.

[11] Satisfactory oxidation to Ir(IV) was achieved with this solution with less interference from the Cl_2 absorption band than was the case in the previous studies[2,4] where saturated Cl_2 solutions were used.

Cl_2 solution which was also 2.5 *F* in $HClO_4$ and 1.2 *F* in $NaClO_4$,[12] allowing 10–20 min for oxidation.

During aquation, anation, and isomerization runs the spectra of reaction solutions were scanned at various times on a Cary Model 11 spectrophotometer at 20–25°, both before and after oxidation with Cl_2, to search for isosbestic points.

In all spectrophotometry the reference cell was filled with identical solution except for the absence of Ir species and added Cl^- or NO_3^-.

Chloride-Release Determinations.—In some aquation runs, Cl^- released was titrated in the presence of Ir species by the Clarke method.[13] In preparing the reaction solutions for titration by reduction of acidity with solid $NaHCO_3$, it must be added very slowly; otherwise some release of ligand Cl^- appears to occur owing to local base hydrolysis and the results are erratic.

Results

Spectra of New Iridium Complexes.—Figure 1 presents the near-ultraviolet and visible absorption spectra of the Ir(III) complexes *trans*- and *cis*-$Ir(OH_2)_2Cl_4^-$ and 1,2,6- and 1,2,3-$Ir(OH_2)_3Cl_3$ in 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$. Spectra of the analogous Ir(IV) complexes in the same medium, but 0.1-saturated with Cl_2, are given in Figure 2; the spectra are corrected for absorption by Cl_2. The absorption maxima and minima are given in Table I.

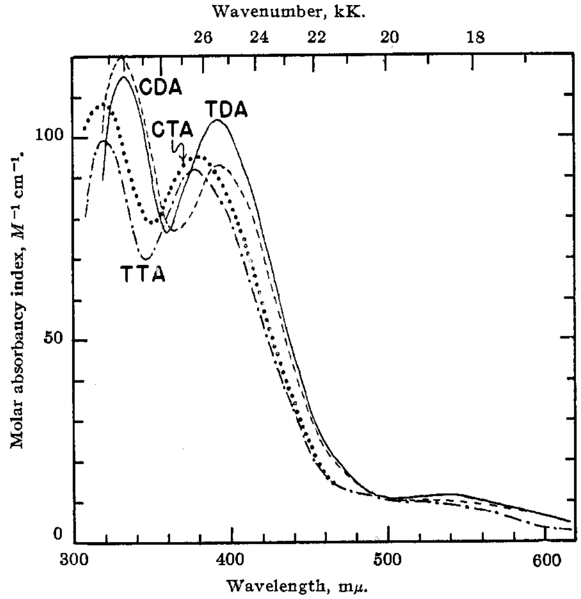

Figure 1.—Visible absorption spectra of aquochloro complexes of iridium(III) in 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$ at 20–25°: CDA, *cis*-$Ir(OH_2)_2Cl_4^-$; TDA, *trans*-$Ir(OH_2)_2Cl_4^-$; CTA, 1,2,3-$Ir(OH_2)_3Cl_3$; TTA, 1,2,6-$Ir(OH_2)_3Cl_3$.

Spectra of the *trans*-diaquo and 1,2,6-triaquo Ir(III) and Ir(IV) complexes are substantially the same[14] as those reported by Chang and Garner[4] for their diaquo and triaquo complexes of unknown geometric configuration, indicating their isomers are the *trans*-diaquo and 1,2,6-triaquo isomers (see Discussion).

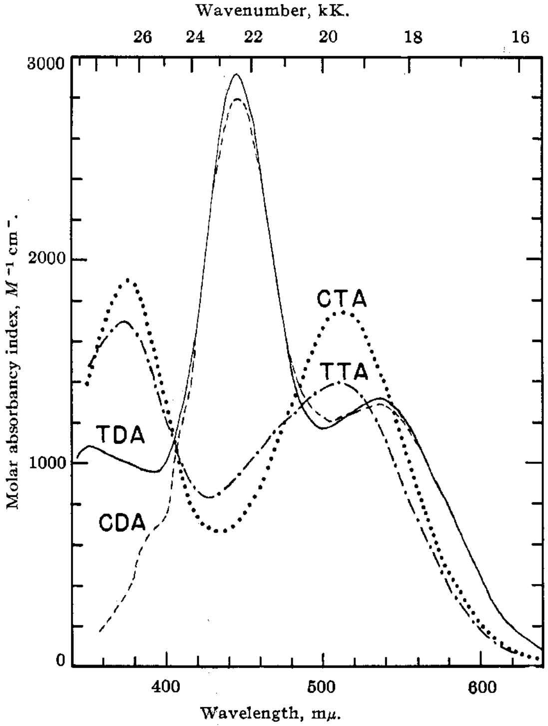

Figure 2.—Visible absorption spectra of aquochloro complexes of iridium(IV) in 0.1-saturated Cl_2–2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$ at 20–25°: CDA, *cis*-$Ir(OH_2)_2Cl_4$; TDA, *trans*-$Ir(OH_2)_2Cl_4$; CTA, 1,2,3-$Ir(OH_2)_3Cl_3^+$; TTA, 1,2,6-$Ir(OH_2)_3Cl_3^+$.

Rate of Aquation of *trans*-$Ir(OH_2)_2Cl_4^-$.—Because changes in optical absorbancy with time are small for the Ir(III) state (see Figure 1) during aquation of *trans*-$Ir(OH_2)_2Cl_4^-$, the aquation was followed spectrophotometrically by oxidizing aliquots of reaction solution to the Ir(IV) state, where absorbancy changes are large at 440 and 460 mμ (see Figure 2). In terms of the absorbancies A_0, A, and A_∞ (at 440 and 460 mμ) at time zero, reaction time t, and 100% reaction (calculated from spectrum of 1,2,6-$Ir(OH_2)_3Cl_3$), respectively, the first-order rate equation is

$$2.303 \log [(A_0 - A_\infty)/(A - A_\infty)] = k_{3T}t \qquad (6)$$

For runs with Cl^- initially absent, plots of this logarithmic function *vs.* t gave good straight lines as far as followed (30–60% reaction), except for several runs taken to 70%, where curvature in a direction corresponding to back reaction was noted.

Titrimetric determination of Cl^- released in reaction 3 allowed computing the molar concentration C of reactant at time t in terms of its initial molarity C_0: $C = C_0 - (Cl^-)$. A good linear plot of ln (C_0/C) *vs.* t was obtained as far as followed (25% reaction).

Values of k_{3T} so obtained are given in Table II. For the spectrophotometric method each value of k_{3T} given is a weighted average of the 440- and 460-mμ values, which usually agreed within 5–15%. In some runs NaH_2PO_4 was used in place of $NaHSO_4$ to elute the *trans*-diaquo reactant used; in some early experiments, a rate acceleration in the presence of HSO_4^- and NO_3^- was noted, and it was desired to examine the rate in the absence of both of these ions. Rates were essentially the same in the HSO_4^- and $H_2PO_4^-$ solutions.

[12] Stock solution was prepared by passing Cl_2 for 20 min into 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$ and then diluting 10-fold with 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$.

[13] F. E. Clarke, *Anal. Chem.*, **22**, 553 (1950).

[14] In a total of 10–12 solutions our *trans*-$Ir(OH_2)_2Cl_4^-$ exhibits a minimum at 502 rather than 510 mμ and has molar absorbancy indices 2–3% larger at the 333- and 392-mμ peaks and 10% smaller at the 530-mμ peak. The other spectra agree almost exactly.

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] (300–600 mμ) at 20–25°

Complex	λ, mμ	a_M, M^{-1} cm^{-1} [b]
trans-$Ir(OH_2)_2Cl_4^-$	333 (max)	115
	360 (min)	76.4
	392 (max)	103
	502 (min)	10.2
	530 (max)	11.3
cis-$Ir(OH_2)_2Cl_4^-$	332 (max)	120
	365 (min)	77.7
	393 (max)	92.8
	505–545 (plat)	10
1,2,6-$Ir(OH_2)_3Cl_3$	320 (max)	99.1
	348 (min)	70.1
	378 (max)	92.0
	~520 (sh)	10
1,2,3-$Ir(OH_2)_3Cl_3$	320 (max)	118
	350 (min)	78.9
	380 (max)	95.5
trans-$Ir(OH_2)_2Cl_4$	350 (max)	1090
	395 (min)	980
	445 (max)	2900
	500 (min)	1170
	535 (max)	1310
cis-$Ir(OH_2)_2Cl_4$	~390 (sh)	~700
	445 (max)	2790
	505 (min)	1200
	535 (max)	1290
1,2,6-$Ir(OH_2)_3Cl_3^+$	375 (max)	1700
	428 (min)	830
	510 (max)	1400
1,2,3-$Ir(OH_2)_3Cl_3^+$	375 (max)	1900
	432 (min)	662
	512 (max)	1750

[a] Solutions of Ir(IV) complexes and their reference solutions were 0.1-saturated Cl_2–2.5 F $HClO_4$–1.2 F $NaClO_4$. [b] The molar absorbancy index a_M (extinction coefficient ϵ) is related to the optical absorbancy A by $A = \log (I_0/I) = a_M cd$ at a given wavelength, where c is the molarity of the complex and d is the optical path in cm.

Aquation of *trans*-$Ir(OH_2)_2Cl_4^-$ in the Presence of NO_3^-.—The above-mentioned increase in aquation rate of *trans*-$Ir(OH_2)_2Cl_4^-$ in the presence of NO_3^- led us to study the rate as a function of the NO_3^- ion formal concentration, (NO_3^-), spectrophotometrically at 440 and 460 mμ and by Cl^- titration. The results are given in Table III, where k_{3N} is the apparent first-order rate constant in the rate law $-d(trans\text{-}Ir(OH_2)_2Cl_4^-)/dt = k_{3N}(trans\text{-}Ir(OH_2)_2Cl_4^-)$ at a given initial formality of NO_3^- ion;[15] each k_{3N} value is a weighted average of values obtained from the 440- and 460-mμ measurements, which nearly always agreed within 5–10%. The spectrophotometric rate constants were calculated as for the runs in the absence of NO_3^-, using A_∞ calculated from the spectrum of 1,2,6-$Ir(OH_2)_3Cl_3^+$ in the absence of NO_3^-.[16] Good first-order rate plots were obtained as far as the reaction was followed (30–60%), except for a few runs taken to 70% reaction,

Table II

First-Order Rate Constants for Aquation of *trans*-$Ir(OH_2)_2Cl_4^-$ in Initially Cl^--Free 2.5 F $HClO_4$–1.2 F $NaClO_4$

Temp, °C	C_0, mF	(HSO_4^-), F	$(H_2PO_4^-)$, F	μ,[a] F	10^6k_{3T}, sec^{-1}
50.00	0.517	...	0.13	3.83	0.48 ± 0.02[b]
50.00	0.995	...	0.25	3.95	0.49 ± 0.01[b]
50.00	0.512	0.15	...	3.85	0.58 ± 0.02[b]
65.00	0.525	...	0.13	3.83	3.6 ± 0.1[b]
65.00	0.995	...	0.25	3.95	3.8 ± 0.1[b]
65.00	1.06	⩽0.007[f]	...	3.70	3.6 ± 0.1[b]
65.00	0.492	0.15	...	3.85	3.7 ± 0.1[b]
65.00	0.674	0.15	...	3.85	4.1 ± 0.1[b]
80.00	0.246	...	0.05	3.75	29 ± 1[b]
80.00	0.470	...	0.10	3.80	30 ± 1[b]
80.00	0.970	...	0.20	3.90	31 ± 1[b]
80.00	1.22	...	0.25	3.95	31 ± 1[b]
80.00	0.260	0.060	...	3.76	28 ± 1[b]
80.00	0.419	0.20	...	3.90	24 ± 1[c]
80.00	1.53	0.20	...	3.90	25 ± 1[c]
80.00	0.379	0.25	...	3.95	32 ± 1[c]
80.00	1.94	0.25	...	3.95	31 ± 1[c]
80.00	5.13	0.30	...	4.00	35 ± 1[c,d]
80.00	1.17	0.12	...	3.82	26 ± 1[c,e]

[a] Ionic strength. [b] Errors are standard deviations obtained by least squaring. [c] Errors are estimated standard deviations. [d] Cl^- release method; all others by spectrophotometric method. [e] $(H^+) = 1.00$ F. [f] Most of HSO_4^- removed by precipitation of $BaSO_4$ with $Ba(ClO_4)_2$.

Table III

Apparent First-Order Rate Constants for Aquation of *trans*-$Ir(OH_2)_2Cl_4^-$ in the Presence of NO_3^- in Initially Cl^--Free $HClO_4$–$NaClO_4$ Solutions

Temp, °C	C_0, mF	(H^+), F	(NO_3^-), F	(HSO_4^-), F	μ,[a] F	10^6k_{3N}, sec^{-1}
50.00	2.81	2.50	0.150[b]	...	3.85	2.14 ± 0.06[c]
50.00	3.58	2.50	0.150[b]	...	3.85	2.16 ± 0.08[c]
50.00	0.710	2.50	0.150[b]	0.15	4.00	1.84 ± 0.12[c]
50.00	4.90	2.50	0.150[b]	0.15	4.00	2.02 ± 0.04[c]
50.00	0.690	2.40	0.300[d]	0.13	3.73	3.58 ± 0.11[e]
50.00	0.690	2.40	0.500[d]	0.13	3.73	4.98 ± 0.15[e]
50.00	0.690	2.40	0.800[d]	0.13	3.73	7.96 ± 0.24[e]
50.00	0.690	2.40	1.00[d]	0.13	3.73	9.36 ± 0.28[e]
65.00	0.680	2.50	0.007[b]	0.15	3.85	4.34 ± 0.08[c]
65.00	0.675	2.50	0.067[b]	0.15	3.92	7.42 ± 0.08[c]
65.00	0.690	2.40	0.100[d]	0.13	3.73	9.36 ± 0.28[e]
65.00	0.675	2.50	0.158[b]	0.15	4.01	11.9 ± 0.2[c]
65.00	0.701	2.40	0.300[d]	0.24	3.84	19.2 ± 0.6[e]
65.00	0.701	2.40	0.500[d]	0.24	3.84	28.7 ± 0.9[e]
65.00	0.690	2.40	0.750[d]	0.13	3.68	38.5 ± 1.2[e]
65.00	0.701	2.40	1.00[d]	0.24	3.84	52.6 ± 1.6[e]
65.00	0.690	2.40	1.15[d]	0.13	3.68	58.8 ± 1.7[e]
80.00	0.692	2.40	0.050[d]	0.25	3.78	34.3 ± 1.0[e]
80.00	1.94	2.35	0.050[d]	0.25	3.77	38.5 ± 1.2[e]
80.00	0.690	2.40	0.100[d]	0.13	3.73	43.7 ± 1.3[e]
80.00	1.94	2.35	0.101[d]	0.25	3.82	45.3 ± 1.4[e]
80.00	1.53	2.50	0.102[d]	0.20	3.88	44.8 ± 1.3[e]
80.00	0.692	2.40	0.150[d]	0.13	3.68	51.9 ± 1.6[e]
80.00	4.98	2.50	0.150[b]	0.15	4.15	51.7 ± 1.6[e]
80.00	4.98	2.50	0.15[b]	0.15	4.15	55 ± 3[e,f]
80.00	0.379	2.35	0.15[d]	0.25	3.78	55.8 ± 3.0[e,f]
80.00	0.379	2.35	0.161[d]	0.25	3.88	64.3 ± 1.9[e]
80.00	0.690	2.40	0.200[d]	0.13	3.73	71.5 ± 2.2[e]
80.00	1.53	2.50	0.201[d]	0.20	3.90	71.3 ± 2.1[e]
80.00	0.419	2.50	0.202[d]	0.20	3.90	74.9 ± 2.3[e]
80.00	0.692	2.40	0.300[d]	0.13	3.73	89.2 ± 2.7[e]
80.00	0.419	2.50	0.406[d]	0.20	3.91	106 ± 3[e]
80.00	0.692	2.40	0.500[d]	0.13	3.73	131 ± 4[e]
80.00	0.690	1.20	0.500[d]	0.13	3.83	129 ± 4[e]
80.00	0.690	3.20	0.500[d]	0.13	3.83	120 ± 4[e]
80.00	0.692	2.40	0.900[d]	0.13	3.83	217 ± 7[e]
80.00	2.92	1.00	0.98[d]	0.12	3.62	223 ± 22[e,f]
80.00	0.692	2.40	1.00[d]	0.13	3.73	234 ± 7[e]

[a] Ionic strength, adjusted with $NaClO_4$. [b] Added as $NaNO_3$. [c] Errors are standard deviations obtained by least squaring. [d] Added as HNO_3. [e] Errors are estimated standard deviations. [f] Cl^- release method; all others by spectrophotometric method.

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(15) Initial and final concentrations of NO_3^- are essentially the same in all runs except the 0.007 F NO_3^- run, since in all other runs the total formality of Ir species is small relative to (NO_3^-).

(16) Since the spectra of *trans*-$Ir(OH_2)_2Cl_4$ and 1,2,6-$Ir(OH_2)_3Cl_3^+$ in the 420–480-mμ region are not significantly affected by NO_3^-, this introduces only a few per cent error in the absorbancies at later reaction times.

where curvature was noted in a direction equivalent to a back reaction.

Figure 3 shows the dependence of k_{3N} on (NO_3^-).

A typical change in spectrum with time for reaction at 80.00° in 2.4 F $HClO_4$–0.13 F $NaHSO_4$–1.00 F $NaNO_3$ is shown in Figure 4.

Rate of Aquation of *cis*-$Ir(OH_2)_2Cl_4^-$.—Aquation of the *cis*-diaquo complex was examined only at 80.00° in 2.4 F $HClO_4$–1.2 F $NaClO_4$–0.3 F $NaHSO_4$ at C_0 = 0.431 mF, using the spectrophotometric method. In the rate law $-d(cis\text{-}Ir(OH_2)_2Cl_4^-)/dt = k_{3C}(cis\text{-}Ir(OH_2)_2Cl_4^-)$, assumed to hold since rate plots were accurately first order over 60% reaction, $k_{3C} = (2.56 \pm 0.07) \times 10^{-5}$ sec^{-1} ($t_{1/2}$ = 7.5 hr) was obtained as an average of values based on 440- and 460-mμ data (which agreed to <1%).

Rate of Cl^- Anation of 1,2,6-$Ir(OH_2)_3Cl_3$.—The anation was followed only spectrophotometrically inasmuch as it was necessarily carried out at Cl^- concentrations much larger than the initial concentration C_0 of the triaquo reactant. Aliquots were oxidized to Ir(IV) with Cl_2, and rate measurements at 420, 440, and 460 mμ were analyzed, using eq 6 with k_{3T} replaced by k'_{-3T} and A_∞ calculated from the spectrum of *cis*-$Ir(OH_2)_2Cl_4$ (see Discussion); in terms of the rate law $-d(1,2,6\text{-}Ir(OH_2)_3Cl_3)/dt = k'_{-3T}(1,2,6\text{-}Ir(OH_2)_3Cl_3) = k_{-3T}(Cl^-)(1,2,6\text{-}Ir(OH_2)_3Cl_3)$. Good pseudo-first-order rate plots were obtained as far as followed (27–49% reaction) at a given (Cl^-). Values of k'_{-3T} from the three wavelengths agreed in each run with a weighted average within 2–8%. Table IV gives the second-order rate constants k_{-3T}, calculated from $k'_{-3T}/(Cl^-)$, where (Cl^-) was set equal to the formal concentration of Cl^-. A best value of k_{-3T} was obtained at each temperature from the slope of a plot of k'_{-3T} *vs.* (Cl^-), which was essentially linear including the origin (k'_{-3T} = 0 when (Cl^-) = 0).

Aquation and Isomerization of 1,2,3-$Ir(OH_2)_3Cl_3$.—In a single experiment, 1,2,3-$Ir(OH_2)_3Cl_3$ (C_0 = 0.4 mF) in 2.4 F $HClO_4$–1.2 F $NaClO_4$ was kept at 90.0° for 24 hr and the visible absorption spectrum of Cl_2-oxidized aliquots scanned at intervals. The zero-time and 2-hr scans gave isosbestic points in excellent agreement with those predicted from Figure 2 for the 1,2,3-$Ir(OH_2)_3Cl_3^+$–1,2,6-$Ir(OH_2)_3Cl_3^+$ system, indicating the occurrence of isomerization (the third scan, at 4 hr, gives isosbestic points which almost agree with those for the first two scans). In subsequent scans the spectral changes suggested concurrent aquation and isomerization. From the absorbancies at 430 and 510 mμ for the first two scans and values of A_∞ calculated from the spectrum of 1,2,6-$Ir(OH_2)_3Cl_3^+$, and assuming a first-order rate law, we obtain $t_{1/2} \sim$ 12 hr at 90.0° (the 430- and 510-mμ values differ by 20%). At 80° a reasonable estimate is $t_{1/2} \sim$ 35–60 hr, approximately 5–8 times $t_{1/2}$ for aquation of *cis*- and *trans*-$Ir(OH_2)_2Cl_4^-$ at 80°. In accord with the constancy of isosbestic points observed during aquation of the diaquo complexes, the estimate indicates little or no effect of the isomerization (and subsequent aquation) on the rate calculations for aquation of the diaquo species.

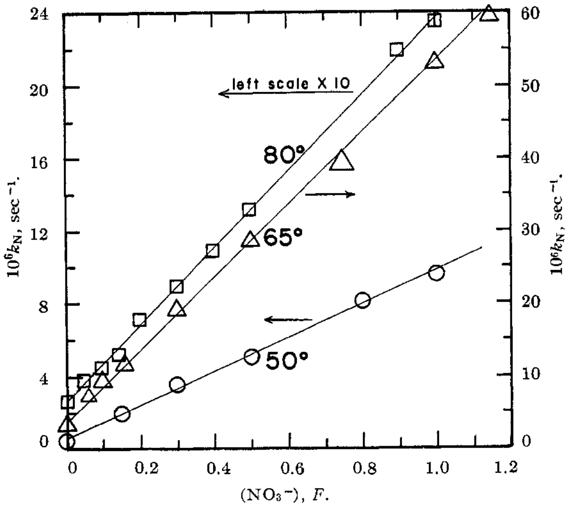

Figure 3.—Rate of aquation of *trans*-$Ir(OH_2)Cl_4^-$ in 1–3 F $HClO_4$ in the presence of NO_3^- (μ = 3.6–4.2, $NaClO_4$) in the dark.

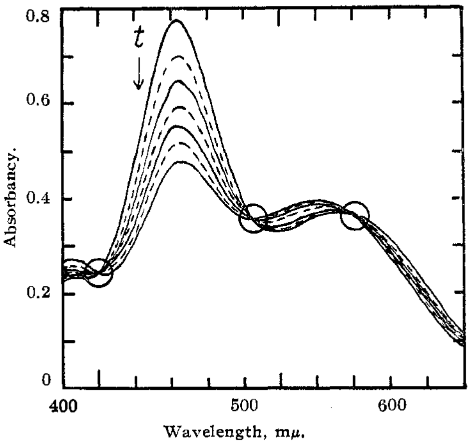

Figure 4.—Change in absorption spectrum with time during aquation of *trans*-$Ir(OH_2)_2Cl_4^-$ in 2.4 F $HClO_4$–1.2 F $NaClO_4$–1.0 F $NaNO_3$–0.1 F $NaHSO_4$ at 80.0°: reading downward at 440 mμ, reaction time is 0, 10, 20, 30, 40, 50, and 60 min.

TABLE IV

SECOND-ORDER RATE CONSTANTS FOR Cl^- ANATION OF 1,2,6-$Ir(OH_2)_3Cl_3$ IN 2.40 F $HClO_4$ (C_0 = 0.495 mF)

Temp, °C	(Cl^-), F	μ,[a] F	10^5k_{-3T}, M^{-1} sec^{-1}
50.00	0.300	3.70	2.3 ± 0.2[b]
50.00	1.00	3.70	2.1 ± 0.2[b]
50.00	1.00	3.60	2.2 ± 0.2[b]
60.00	0.300	3.70	8.1 ± 0.8[b]
60.00	1.00	3.70	8.9 ± 0.9[b]

[a] Ionic strength adjusted with $NaClO_4$. [b] Errors are estimated standard deviations.

Aquation of 1,2,6-$Ir(OH_2)_3Cl_3$.—In a single experiment like that above, except with 0.5 mF 1,2,6-$Ir(OH_2)_3Cl_3$, the spectral changes gave no indication of any isomerization at 90°. Instead there was a slow change suggesting aquation.

Discussion

Spectra.—Figure 1, together with Figure 1 of ref 4, indicates that the d–d absorption bands of the Ir(III) complexes $IrCl_6^{3-}$, $Ir(OH_2)Cl_5^{2-}$, *cis*- and *trans*-$Ir(OH_2)_2Cl_4^-$, and 1,2,3- and 1,2,6-$Ir(OH_2)_3Cl_3$ are progressively displaced toward shorter wavelengths, and increase in intensity of the shorter wavelength band relative to the longer wavelength band occurs as the number of ligand water molecules per Ir increases. The displacement is in the direction expected from the order of increasing ligand field, $Cl^- < H_2O$, in the spectrochemical series. Spectra of the Ir(III) diaquo isomers are similar, except for the presence of the low-intensity 530-mμ band and greater relative intensity of the 392-mμ band in the *trans* isomer. The Ir(III) triaquo isomers are even more similar in their spectra, the main difference being the appreciably greater ratio of 378–380-mμ to 320-mμ peak-height intensities in the 1,2,6 isomer.

Figure 2, together with Figure 2 of ref 4, shows the absorption spectra of the corresponding Ir(IV) complexes. The high values of molar absorbancy indices at the absorption maxima indicate that these bands arise from charge transfer, and so we neither expect nor find the type of correlation exhibited above by the Ir(III) complexes.

Assignment of Geometric Configurations.—The diaquo and triaquo species can each exist in two geometric configurations. Each has a plane of symmetry and is incapable of existing in optically active forms, so the criterion of resolution of optical enantiomers (often used to characterize a *cis* isomer) is not applicable here. Although the symmetry difference between such isomers often leads to a useful criterion based on the number of bands and their intensities in the visible absorption spectra, the spectra of each pair of isomers here are too similar to allow assignments on that basis.

Instead, our assignments have been made for the Ir(III) complexes on the relative ease of elution in anion-exchange chromatography. As a general rule the *trans* isomer (more generally, the isomer having the smaller electric dipole moment) is eluted first.[17] So far as is known to the authors, no exception to this "rule" has been observed. Assignments of $Ru(OH_2)_3Cl_3$ and $Ru(OH_2)_2Cl_4^-$ isomers made on this basis[18] have recently been confirmed, respectively, by dipole moment determinations[19,20] and by an X-ray diffraction study[21] of $[As(C_6H_5)_4][Ru(OH_2)_2Cl_4]\cdot H_2O$.

The assignments given in this paper are supported by our observations that the $Ir(OH_2)_2Cl_4^-$ isomer to which we have assigned a *trans* configuration aquates to give apparently 100% 1,2,6-$Ir(OH_2)_3Cl_3$ (the *trans* isomer can give only this product unless rearrangement accompanies the aquation), whereas the $Ir(OH_2)_2Cl_4^-$ isomer we infer to be the *cis* form aquates to give *ca.* 60% 1,2,3- and 40% 1,2,6-$Ir(OH_2)_3Cl_3$ (in the absence of isomerization, the *cis*-diaquo complex would be expected on purely statistical grounds to give 45–50% 1,2,3 product) (see below).

An attempt to make *cis*-$Ir(OH_2)_2Cl_4^-$, in further support of our assignments, was made by preparing $Ir(C_2O_4)Cl_4^{3-}$ by the method of Duffour[22] and trying to convert it to the diaquo (presumably *cis*) complex by treatment with MnO_4^- at 40–50° for 1–2 hr or with Ca^{2+} at 25° for 2 days; under the conditions tried, the oxalato complex remained essentially unchanged. An attempt to $C_2O_4^{2-}$-anate *trans*-$Ir(OH_2)_2Cl_4^-$ in a solution 1 *F* in $Na_2C_2O_4$, 2.5 *F* in $HClO_4$, and 0.2 *F* in $NaClO_4$ resulted in no apparent change in 1 day at 25°, and in 0.5–2 hr at 80° there appeared to be some $C_2O_4^{2-}$ anation but this was accompanied by appreciable aquation.

Assignments of configuration for these Ir(III) complexes should apply also to the Ir(IV) state, inasmuch as the species can be readily oxidized and reduced back to the Ir(III) state at room temperature without apparent rearrangement.

Aquation of *trans*-$Ir(OH_2)_2Cl_4^-$ in ClO_4^- Medium.—In ClO_4^- medium the aquation occurs according to over-all eq 3 (see Introduction). Spectral scans made during aquation gave good isosbestic points up to 50% reaction. These occurred at 406 ± 3 ($a_M = 1000 \pm 50$), 485 ± 2 ($a_M = 1260 \pm 20$), and 530 ± 3 mμ ($a_M = 1300 \pm 20$ M^{-1} cm^{-1}), in good agreement with the values expected for the *trans*-$Ir(OH_2)_2Cl_4^-$–1,2,6-$Ir(OH_2)_3Cl_3^+$ system from Figure 2: 407 ± 2 ($a_M = 1120 \pm 20$), 487 ± 2 ($a_M = 1280 \pm 20$), and 528 ± 2 mμ ($a_M = 1290 \pm 20$ M^{-1} cm^{-1}). The 407-mμ data are only approximate because of some interference from Cl_2 absorption imbalances. The observed isosbestic points are distinctly different from those expected for aquation to 1,2,3-$Ir(OH_2)_3Cl_3$ (see Figure 2), and behavior in the 510-mμ region also appears to exclude the presence of any significant amount of 1,2,3 product. This stereochemical result is the expected result if there is no rearrangement, and the latter is ruled out during the aquation by the existence and values of the isosbestic points and supported by the agreement found between rate constants obtained from spectrophotometric and Cl^--release measurements and by our finding no evidence for isomerization of 1,2,6-$Ir(OH_2)_3Cl_3$ in a single experiment designed to search for it.

In 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$ at 50.00° $k_{3T} = (5.1 \pm 0.2) \times 10^{-7}$ sec^{-1} ($t_{1/2}$ = 380 hr), essentially independent of C_0 from 0.5 to 1 m*F*. At 80.00° conditions were varied to a greater extent, and $k_{3T} = (2.9 \pm 0.8) \times 10^{-6}$ sec^{-1}, essentially independent of C_0 from 0.2 to 5 m*F* and of (H^+) from 1.0 to 2.5 *F* ($\mu = 3.8$–4.0, $NaClO_4$ plus small amounts of HSO_4^- or $H_2PO_4^-$).

A plot of ln k_{3T} *vs.* $1/T$ for the 50, 65, and 80° best values was linear and corresponds to $E_a = 30.5 \pm 0.9$ kcal and log $pZ = 14.3 \pm 0.4$ (sec^{-1}). Extrapolation to 25° gives $k_{3T} \sim 8 + 10^{-9}$ sec^{-1}.

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[17] See J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 200, and references therein.

[18] R. E. Connick and D. A. Fine, *J. Am. Chem. Soc.*, **83**, 3414 (1961).

[19] E. E. Mercer and W. A. McAllister, *Inorg. Chem.*, **4**, 1414 (1965).

[20] We have attempted extraction of $Ir(OH_2)_3Cl_3$ isomers into organic solvents for dipole moment measurements, but without success.

[21] T. E. Hopkins, A. Zalkin, D. H. Templeton, and M. G. Adamson, *Inorg. Chem.*, **5**, 1427 (1966).

[22] A. Duffour, *Compt. Rend.*, **152**, 1393 (1911); *Ann. Chim. Phys.*, [8] **30**, 188 (1913).

Aquation of *trans*-$Ir(OH_2)_2Cl_4^-$ in NO_3^-–ClO_4^- Medium.—Figure 3 and Table III show that the rate law applicable is

$$-d(trans\text{-}Ir(OH_2)_2Cl_4^-)/dt = k_{3N}(trans\text{-}Ir(OH_2)_2Cl_4^-) = [k_{3T} + k_{3TN}(NO_3^-)](trans\text{-}Ir(OH_2)_2Cl_4^-) \quad (7)$$

Within experimental error the y intercepts of Figure 3 give the same values of k_{3T} obtained in ClO_4^- medium alone. Values of 10^6k_{3TN} calculated from the slopes are 9.1 ± 0.3, 48 ± 2, and 217 ± 7 M^{-1} sec^{-1} at 50.00, 65.00, and 80.00°, respectively.[23] At 80.00°, where conditions were varied most, k_{3TN} is essentially independent of C_0 from 0.4 to 5 mF, of (NO_3^-) from zero to 1.0 F, and of (H^+) from 1.0 to 3.2 F (μ = 3.6–4.2). A good Arrhenius plot was obtained, giving $E_a = 24.0 \pm 0.6$ kcal and $\log pZ = 11.1 \pm 0.3$ (M^{-1} sec^{-1}) for the NO_3^--dependent path. At 25° $k_{3TN} \sim 4 \times 10^{-7}$ M^{-1} sec^{-1} by extrapolation.

Good isosbestic points were found up to 50% reaction, but the positions of two of them were different from those found in ClO_4^- medium alone. In particular, the long-wavelength isosbestic point shifts to progressively longer wavelengths from run to run as (NO_3^-) is increased, amounting to a shift of *ca.* 14 mμ in going from 0 to 1 F NO_3^-. For comparison with the isosbestic points in ClO_4^- medium, Figure 4 shows isosbestic points at 400 ± 3 (a_M = 950 ± 100), 485 ± 2 (a_M = 1290 ± 30), and 542 ± 2 mμ (a_M = 1300 ± 30 M^{-1} cm^{-1}).

The greater reaction rate and the shift in isosbestic points in NO_3^-–ClO_4^- medium cannot be due to oxidation of *trans*-$Ir(OH_2)_2Cl_4^-$. Preliminary experiments on aquation of *trans*-$Ir(OH_2)_2Cl_4$ (obtained by oxidation with $KMnO_4$ at 20–25°) in 2.5 F $HClO_4$–1.2 F $NaClO_4$–0.06 F $NaHSO_4$ indicate that the aquation rate at 65° is no more than one-fourteenth that of the Ir(III) complex under these conditions. Thus, although spectral evidence in reaction solutions containing NO_3^- indicates 1–8% oxidation to *trans*-$Ir(OH_2)_2Cl_4$, the presence of this complex cannot account for a rate acceleration. Moreover, since k_{3TN} is independent of whether the NO_3^- is added as $NaNO_3$ or as HNO_3, the effects observed are due to NO_3^- and not to possible nitrogen oxides or other impurities possibly present in HNO_3.

The NO_3^- term in the rate law (eq 7) and the isosbestic point shifts suggest that a reaction path is involved in which NO_3^- complexes with Ir(III). One possibility is

$$trans\text{-}Ir(OH_2)_2Cl_4^- + NO_3^- \overset{K}{\rightleftharpoons} Ir(OH_2)(NO_3)Cl_4^{2-} + H_2O \text{ (relatively fast equilibrium far to left at 50–80°)} \quad (8a)$$

$$Ir(OH_2)(NO_3)Cl_4^{2-} + H_2O \xrightarrow{k_{8b}} Ir(OH_2)_2(NO_3)Cl_3^- + Cl^- \text{ (rate determining)} \quad (8b)$$

This path is consistent with the observed rate law (with $k_{3TN} = Kk_{8b}$), with the essential agreement of spectrophotometric and Cl^--release values of k_{3TN} and with a shift in isosbestic points. Increase in the magnitude of this shift with increasing (NO_3^-) could be accounted for by an increase in the proportion of aquation going *via* the NO_3^- path. Alternatively, a direct replacement might occur

$$trans\text{-}Ir(OH_2)_2Cl_4^- + NO_3^- \xrightarrow{k_9} Ir(OH_2)_2(NO_3)Cl_3^- + Cl^- \quad (9)$$

with $k_{3TN} = k_9$, although this seems inherently less plausible. Mechanisms involving NO_3^- acting as a bidentate ligand can also be constructed.

The order of increasing ligand field in the spectrochemical series based on Co(III) has been given[24] as $Cl^- < NO_3^- \ll H_2O$, and if this is applicable to Ir(III) complexes, it would predict that substitution of NO_3^- for ligand Cl (in going from *trans*-$Ir(OH_2)_2Cl_4^-$ to the proposed product) would shift the d–d bands to slightly shorter wavelengths. We have not been able to observe such a shift because in the presence of NO_3^- at the reaction temperature 1–8% oxidation occurs, and the high molar absorbancy indices of the Ir(IV) bands (*ca.* 10–30 times greater than for Ir(III)) obscure the d–d bands; attempts to eliminate the Ir(IV) interference by reduction with H_2O_2 gave interference from H_2O_2 absorption below 400 mμ (where the expected bands would lie); moreover, NO_3^- itself interferes below *ca.* 350 mμ. The "NO_3^- isosbestic-point shift" is observed in the Ir(IV) state, where we presumably have charge-transfer spectra. A definite prediction of the direction of such a shift seems unwarranted in the absence of significant spectral information on NO_3^- complexes and the uncertainty of whether NO_3^- is acting here as a unidentate or bidentate ligand. At room temperature, NO_3^- (even up to 1 F) has essentially no effect on the visible absorption spectra of the *cis*- and *trans*-diaquo and 1,2,3- and 1,2,6-triaquo complexes, either in the Ir(III) or Ir(IV) state, and at 50–80° the spectral changes require time. Hence, the spectral changes observed at 50–80° in the reaction solutions containing NO_3^- are not due to ion-pairing effects, but presumably to NO_3^- complexing with Ir(III).

Attempts to isolate such an NO_3^- complex by anion-exchange chromatography were unsuccessful, as was an attempt to precipitate the Ag^+ salt of the hypothetical NO_3^- complex and obtain an NO_3^-:Ir ratio on it (too much coprecipitation of NO_3^- from the reaction solutions).

Acceleration of *trans*-$Ir(OH_2)_2Cl_4^-$ aquation in the presence of NO_3^- raises the question of possible similar NO_3^- paths for $IrCl_6^{3-}$ and $Ir(OH_2)Cl_5^{2-}$ aquation (NO_3^- was absent from the aquation solutions in the studies[2,4] of $IrCl_6^{3-}$ and $Ir(OH_2)Cl_5^{2-}$). We have found that both $IrCl_6^{3-}$ and $Ir(OH_2)Cl_5^{2-}$ are oxidized to an apparent steady-state extent of 20–30% in 0.1 F $NaNO_3$–1 F $HClO_4$ within 5 min at 20–25°, complicating any attempt to search for NO_3^--dependent aquation paths.

Aquation of *cis*-$Ir(OH_2)_2Cl_4^-$.—In 2.4 F $HClO_4$–1.2

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[23] In a single preliminary experiment, Chang and Garner[4] obtained $k_{3N} = 2.9 \times 10^{-5}$ sec^{-1} at 50.00° for aquation of what is now characterized as *trans*-$Ir(OH_2)_2Cl_4^-$. Because of their chromatographic procedure, their reactant solution was actually *ca.* 0.15 F in (NO_3^-), as well as 2.5 F in $HClO_4$ and 1.2 F in $NaClO_4$. Their spectrophotometric value then corresponds to $10^6k_{3TN} \approx 16$ and their Cl^--release value (obtained in *ca.* 0.3 F NO_3^-) gives $10^6k_{3TN} \approx 8$, which is of the same order of magnitude as our accurate k_{3TN} value.

[24] Reference 17, p 266.

F $NaClO_4$–0.3 *F* $NaHSO_4$ at 80°, spectral scans made on Cl_2-oxidized aliquots during aquation of *cis*-$Ir(OH_2)_2Cl_4^-$ exhibit good isosbestic points up to 40% reaction. These occur at 408 ± 2 ($a_M = 1030 \pm 30$), 485 ± 2 ($a_M = 1370 \pm 30$), and 540 ± 2 mμ ($a_M = 1300 \pm 30$ M^{-1} cm^{-1}), which are not in accord with aquation to either 1,2,3- or 1,2,6-$Ir(OH_2)_3Cl_3$ alone. Trial-and-error plottings, however, show that aquation of *cis*-$Ir(OH_2)_2Cl_4^-$ to a 60% 1,2,3- and 40% 1,2,6-$Ir(OH_2)_3Cl_3$ mixture would give within experimental error the isosbestic points actually observed. On a purely statistical basis, aquation of *cis*-$Ir(OH_2)_2Cl_4^-$ *via* a dissociation mechanism through a square-pyramid or trigonal-bipyramid transition state would be expected to give 50% 1,2,3 and 50% 1,2,6 product; *via* an association mechanism through a pentagonal-bipyramid transition state, 44.5% 1,2,3 and 55.5% 1,2,6 product would be expected. However, prediction of product ratios from purely statistical considerations is almost certainly not very meaningful because electrostatic and steric effects must also influence the stereochemistry; *e.g.*, if a strong *trans* effect were operative here (Cl *trans* to a Cl replaced by H_2O more readily than Cl *cis* to a Cl), the aquation product would be expected to be predominantly, or even wholly, 1,2,3-$Ir(OH_2)_3Cl_3$. In this sense, the actual stereochemical result may imply the presence of some *trans* effect in this aquation.

Cl^- Anation of 1,2,6-$Ir(OH_2)_3Cl_3$.—Spectral scans made during Cl^- anation of 1,2,6-$Ir(OH_2)_3Cl_3$ exhibited only poorly defined isosbestic points in the regions expected for conversion to *cis*- or *trans*-$Ir(OH_2)_2Cl_4^-$ or a mixture of these. Because of interference from some $Ir(OH_2)Cl_5^{2-}$ formed in the presence of the high concentrations of Cl^-, it is not possible to obtain the isomeric distribution of diaquo product from the spectral changes.

From the best values of k_{-3T} for the anation (eq 5) at 50.00 and 60.00°, namely, (2.2 ± 0.2) × 10^{-5} and (8.2 ± 0.8) × 10^{-5} M^{-1} sec^{-1}, and assuming an Arrhenius temperature dependence, we obtain E_a = 28.8 ± 0.6 kcal and log pZ = 14.7 ± 0.3 (M^{-1} sec^{-1}). By extrapolation to 25°, $k_{-3T} \sim 5 \times 10^{-7}$ M^{-1} sec^{-1}. In 2.4–2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$ at 50° the second-order Cl^- anation rate constants are in the ratio $k_{-1}:k_{-2}:k_{-3T}$ = 1.0:0.61:0.20 for the series $Ir(OH_2)Cl_5^{2-}$,[2] *trans*-$Ir(OH_2)_2Cl_4^-$,[4] and 1,2,6-$Ir(OH_2)_3Cl_3$. Although E_a is not known for Cl^- anation of $Ir(OH_2)Cl_5^{2-}$, this rate decline appears to arise mainly from an increase in E_a, perhaps owing to an expected increase in crystal-field contribution to E_a with increasing replacement of ligand Cl by ligand H_2O.

At 50° in the same medium, aquation rates in the series $IrCl_6^{3-}$,[2,25] $Ir(OH_2)Cl_5^{2-}$,[4] and *trans*-$Ir(OH_2)_2Cl_4^-$ decrease as follows: $k_1:k_2:k_{3T}$ = 1.0:0.067:0.037. Robb and Harris[26] have recently studied the aquation of $RhCl_6^{3-}$ and Cl^- anation of $Rh(OH_2)Cl_5^{2-}$ (and have reported that preliminary experiments show the aquation of the latter is at least 10 times slower) and find the system to parallel closely the behavior of the Ir(III) system, but with rates about 100 times greater. A similar parallel appears to exist with the $RuCl_6^{3-}$–$Ru(OH_2)Cl_5^{2-}$ system,[27] where the aquation rates are still greater.

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[25] V. I. Krantsov and G. M. Petrova, *Zh. Neorgan. Khim.*, **9**, 1010 (1964), through *Chem. Abstr.*, **61**, 73*c* (1964), find essentially the same $IrCl_6^{3-}$ aquation rate constant from measurements of the change with time of the emf of an $IrCl_6^{3-}$–$IrCl_6^{2-}$ couple in 2 *F* HCl at 50°.

[26] W. Robb and G. M. Harris, *J. Am. Chem. Soc.*, **87**, 4472 (1965).

[27] R. E. Connick and M. G. Adamson, Abstract No. 9, Division of Inorganic Chemistry, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 13–17, 1965.