$$\frac{r\Delta U}{e^2} = \sum_1^\infty (-1)^n \Big[- \left(\frac{1}{n + \Delta_1}\right) - \left(\frac{1}{n + \Delta_2}\right) + \left(\frac{1}{n + \Delta_1 + 2\Delta_2}\right) + \left(\frac{1}{n + 2\Delta_1 + \Delta_2}\right) + \left(\frac{-2(1 + \Delta_1 + \Delta_2)}{n + 2\Delta_1 + 2\Delta_2}\right) + \left(\frac{1 + 2\Delta_1}{n + 2\Delta_1}\right) + \left(\frac{1 + 2\Delta_2}{n + 2\Delta_2}\right)\Big] + \frac{1}{1 + \Delta_1 + 2\Delta_2} + \frac{1}{1 + 2\Delta_1 + \Delta_2} - \frac{1}{1 + \Delta_1 + \Delta_2} - \frac{1}{1 + 2\Delta_1 + 2\Delta_2} \quad (4)$$

Calculated values of $\Delta U(\mathrm{NaNO_3}) - \Delta U(\mathrm{KNO_3})$ are listed in Column 6 of Table III and are about 0.7 times the value based on the nearest neighbor calculation. Although these calculations cannot be correct for a real three dimensional system, they serve to assess the importance of long range coulombic interactions. Other effects, as for example a polarization effect, would probably lead to a larger solvent effect for the bromide containing systems. Since the calculated coulombic effect is in the same direction as the observed differences, it is likely that at least part of the effect is coulombic. It is important to note that the relative sizes of both cations *and* both anions enter into this effect. If the solvent anion D^- were smaller than the solute anion C^- and all others ions were the sizes used in the calculation, then the sign of the energy of the "*reciprocal coulombic effect*" would be changed.

Acknowledgments.—We would like to acknowledge the help of Harvey Carter of the Mathematics Panel of the Oak Ridge National Laboratory in making the numerical calculations from equation 4. One of us (J.B.) would like to acknowledge a Cottrell Grant from the Research Corporation and financial assistance from the Department of Industrial Coöperation of the University of Maine.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES 24, CALIFORNIA]

A Thermodynamic and Kinetic Study of Hexachloro and Aquopentachloro Complexes of Iridium(III) in Aqueous Solutions[1]

BY INGEBORG A. POULSEN AND CLIFFORD S. GARNER

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A spectrophotometric study of the kinetics of aquation of $\mathrm{IrCl_6^{-3}}$ and of $\mathrm{Cl^-}$ anation of $\mathrm{Ir(OH_2)Cl_5^{-2}}$ in 1.0–2.5 *F* $\mathrm{HClO_4}$ (or HCl) at 50° has led to evaluation of rate constants and the equilibrium constant *K* for the reversible reaction $\mathrm{IrCl_6^{-3}} + \mathrm{H_2O} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ir(OH_2)Cl_5^{-2}} + \mathrm{Cl^-}$. Aquation of $\mathrm{IrCl_6^{-3}}$ was studied at 6–50° in 1.0–2.5 *F* $\mathrm{HClO_4}$ by a spectrophotometric method and in 1.0 *F* $\mathrm{HClO_4}$ by a titrimetric method. At 25.05° and $\mu = 2.2$, $k_1 = (9.4 \pm 0.6) \times 10^{-6}$ sec.$^{-1}$, $E_a = 30.4 \pm 2.0$ kcal., and log $PZ = 17.5 \pm 1.8$. At 50.05° k_1 is independent of $(\mathrm{IrCl_6^{-3}})_0$ over the range 0.5–11.5 m*F* ($\mu = 2.2$), of $(\mathrm{Cl^-})_0$ over the ranges 0–2.2 *M* ($\mu = 2.2$) and 1.0–3.4 *M* ($\mu = 3.4$), and, in $\mathrm{HClO_4}$, of $(\mathrm{H^+})$ between 1.0–2.5 *M* ($\mu = 3.6$–3.7); k_1 decreases as μ increases from 2.2–3.4. At 1 *M* $\mathrm{H^+}$ and 50.05° the anation rate law was found experimentally to be $-\mathrm{d}(\mathrm{Ir(OH_2)Cl_5^{-2}})/\mathrm{d}t = k_{-1}(\mathrm{Ir(OH_2)Cl_5^{-2}})(\mathrm{Cl^-})$, with $k_{-1} = 5 \times 10^{-5}$ M^{-1} sec.$^{-1}$, approximately independent of μ between 2.2 and 3.4; k_{-1} increases with $(\mathrm{H^+})$ in the range 1.0–2.5 *M* ($\mu = 3.4$–3.7). *K* varies between 2.2 and 9.3 *M* at 50° in these solutions. The first-order rate constant for aquation of $\mathrm{Ir(OH_2)Cl_5^{-2}}$ is $\lesssim 0.1k_1$ at 25 and 50°. A simple new method was developed for the preparation of $\mathrm{Na_3IrCl_6 \cdot 2H_2O}$.

During continued studies[2-4] of hexachloro complexes of iridium(III) and iridium(IV) in this Laboratory a need arose to investigate the aquation of hexachloroiridate(III) anion. The inability of the reversible reactions

$$\mathrm{IrCl_6^{-2} + H_2O \rightleftharpoons Ir(OH_2)Cl_5^- + Cl^-} \quad (1)$$

to account fully for the observed decrease in rate of chloride ion release during aquation of hexachloroiridate(IV) anion at 50°,[4] together with experiments made by us at 115° with $\mathrm{IrCl_6^{-2}}$ in hydrochloric acid solutions either saturated with $\mathrm{Cl_2}$ or $\mathrm{Cl_2}$-free, indicate that reactions 1 in $\mathrm{Cl_2}$-free solutions may in some way be linked to oxidation–reduction reactions, possibly through the reaction sequence

$$\mathrm{IrCl_6^{-2} + Cl^- \rightleftharpoons IrCl_6^{-3} + {}^1/_2Cl_2} \quad (2)$$

$$\mathrm{IrCl_6^{-3} + H_2O \rightleftharpoons Ir(OH_2)Cl_5^{-2} + Cl^-} \quad (3)$$

$$\mathrm{Ir(OH_2)Cl_5^{-2} + {}^1/_2Cl_2 \rightleftharpoons Ir(OH_2)Cl_5^- + Cl^-} \quad (4)$$

Reversible interconversion of $\mathrm{IrCl_6^{-3}}$ and $\mathrm{Ir(OH_2)Cl_5^{-2}}$ *via* reaction 3 has long been known.[5,6] More recently conductometric[7,8] and spectrophotometric[9] methods were employed to study qualitatively the aquation of $\mathrm{IrCl_6^{-3}}$ in aqueous solutions; in the conductometric work acid was not present and the results may have been influenced by base hydrolysis. Except for several isotopic exchange studies and kinetic investigations of the base hydrolysis of hexachloroantimonate(V) anion[10] and aquation of hexachlororuthenate(III) anion,[11] no quantitative kinetic studies appear to have been published on metal hexahalo complexes in aqueous solution.

In the present work we have followed reaction 3 from both sides partly spectrophotometrically

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(1) Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University.

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and partly titrimetrically with the purpose of determining rate laws and calculating reaction rates, equilibrium constants and activation energies. The methods used made it mandatory to investigate the reproducibility of the molar absorbancy indices *a* of the iridium species formed when $IrCl_6^{-3}$ and $Ir(OH_2)Cl_5^{-2}$ solutions are saturated with Cl_2. Values of *a* for $IrCl_6^{-2}$ given in the literature[12–17] vary considerably, whereas no values for $Ir(OH_2)Cl_5^{-}$ apparently have been published. Optical absorbancy data[9,12,13,17,18] for the corresponding iridium(III) ions have been checked experimentally where required.

Experimental

Sodium Hexachloroiridate(IV) 6-Hydrate.—Commercial $(NH_4)_2IrCl_6$ (A. D. MacKay, Inc., New York), found by Pacific SpectroChemical Laboratory, Los Angeles, to contain <0.02% of any of the other Pt metals, was converted to the Na salt as described by Sloth and Garner.[2] The product, instead of being dried after the last precipitation with chloroform, was redissolved in acetone and crystallized by evaporating the acetone in an air stream. The hexahydrated salt formed is not hygroscopic. This salt was used in the spectral studies.

Anal. Calcd. for $Na_2IrCl_6{\cdot}6H_2O$: per cent. oxidation equivalents, 0.1789; H_2O, 19.3. Found: per cent. oxidation equivalents, 0.1748; H_2O, 19.5.

The 2.3% relative deviation between the calculated and found oxidation equivalents may be due to reduction by that amount either during the recrystallization from the acetone or the dissolution in water. Measurements of optical absorbancy showed that a similar extent of reduction occurs when the salt is dissolved in water rather than in 2.5 *F* $HClO_4$ saturated with Cl_2.

Commercial $(NH_4)_2IrCl_6$ (Fairmont Chemical Co., New York) was purified by the procedure of Woo and Yost[19] and converted to the Na salt by boiling with HCl and evaporating the solution to dryness with excess NaCl on the steam bath in an atmosphere of Cl_2. The residue was extracted with acetone and $Na_2IrCl_6{\cdot}6H_2O$ was precipitated with chloroform, filtered, washed with chloroform and dried in air before it was used for the preparation of the various Ir complexes. Analyses by Pacific SpectroChemical Laboratory indicated <0.3% Pt and <0.08% of any of the remaining Pt metals.

Sodium Hexachloroiridate(III) and Its 2-Hydrate.—Ethanolic solutions of $Na_2IrCl_6{\cdot}6H_2O$ (300 ml., 0.03 *F*) and of $NaNO_2$ (100 ml., 0.17 *F*) were made on the steam bath, filtered, then mixed while still hot to give immediate precipitation of $Na_3IrCl_6{\cdot}2H_2O$, which was filtered and washed with warm ethanol. The green powder was kept as the 2-hydrate by storage in a vacuum desiccator over $Mg(ClO_4)_2$; yield ~80%. The 2-hydrate was dehydrated to constant weight in an oven at 120° for ~1.5–3 hr. immediately before analysis.

Anal. Calcd. for Na_3IrCl_6: Ir, 40.54; Cl (as HCl), 22.45; Cl (in ignition residue), 22.45; per cent. reduction equivalents, 0.2110. Found: Ir, 40.87; Cl (as HCl), 22.35; Cl (in ignition residue), 22.16; per cent. reduction equivalents, 0.2097. Calcd. for $Na_3IrCl_6{\cdot}2H_2O$: H_2O, 7.07. Found: H_2O, 7.20.

Both compounds have the characteristic green color and appearance described by Delépine and Boussi.[20] Their observations that a 10-hydrate is formed on exposure to atmospheric air were confirmed.

The above new method of synthesizing $IrCl_6^{-3}$ salts is faster and more convenient than previous methods.[5–7,20–24]

The optical absorbancy of freshly prepared aqueous solutions of Na_3IrCl_6 was found to increase over the range 300–600 mμ with increased time of heating of the salt at 120°; *e.g.*, per cent. increases (relative to unheated $Na_3IrCl_6{\cdot}2H_2O$) for 1.5–3 hr. and several days of heating, respectively, were 0 and 28, 1 and 9, 9 and 27, and 150 and 330 at 560, 415, 357 and 312 mμ, respectively. Decreases in absorbancy (less pronounced) were observed when these solutions were oxidized with Cl_2. No displacement of the absorption maxima and minima accompanied these changes in absorbancy, and no change in weight (<0.1%) was detected. Similar effects were found for $K_3IrCl_6{\cdot}3H_2O$.

Potassium Aquopentachloroiridate(III).—This salt was prepared according to Delépine[5] by reduction of K_2IrCl_6 (synthesized from $Na_2IrCl_6{\cdot}6H_2O$ by precipitation with saturated KCl) with $K_2C_2O_4$. The product was recrystallized twice from hot water and dried in air at room temperature, giving dark yellow-green rhombohedral crystals, stable in air at room temperature; yield ~15%.

Anal. Calcd. for $K_2Ir(OH)_2Cl_5$: Ir, 41.26; Cl (as HCl), 22.85; Cl (in ignition residue), 15.23. Found: Ir, 41.33; Cl (as HCl), 23.18; Cl (in ignition residue), 15.26.

Sodium Perchlorate.—C.P. $NaClO_4$ was found to contain oxidizing impurities. $NaClO_4$ used in this work was made by neutralizing $HClO_4$ (J. T. Baker Analyzed) with C.P. Na_2CO_3.

Other chemicals were C.P. or reagent grade.

Chemical Analyses.—Weighed portions of the complex compounds were reduced to metallic Ir, alkali chloride and HCl by H_2 at 500–600° for 3–3.5 hr., essentially as described earlier,[2] except that the alkali chloride in the residue was separated from the Ir metal by centrifuging 3 times with water. The Ir metal was washed with ethanol and ether, then dried at room temperature.

Per cent. oxidation equivalents was determined by titration with standardized 0.01 *F* $Na_2S_2O_3$ using iodine–starch indicator. Per cent. reduction equivalents was determined potentiometrically by titrating O_2-free solutions of the compound with standardized 0.01 *F* $KMnO_4$. Rh-foil electrodes were found superior to Pt electrodes for this purpose; a Radiometer TTT-1a titrator was used as potentiometer.

Kinetic Runs.—Two different procedures were employed in making the aquation runs with $Na_3IrCl_6{\cdot}2H_2O$. In one the initial concentration of $IrCl_6^{-3}$, $(IrCl_6^{-3})_0$, was ~2 or 10 m*F*, and the solution were made with the 2-hydrate dehydrated to constant weight at 120° for <3 hr. Proper amounts of O_2-free aqueous stock solutions of $HClO_4$, $NaClO_4$ and/or NaCl were mixed, in some cases with fresh constant-boiling HCl, and brought to the run temperature before dissolution of the weighed complex and making up to volume. In the second procedure $(IrCl_6^{-3})_0$ was ~0.5 m*F*, made with $Na_3IrCl_6{\cdot}2H_2O$ dried only at ~25° over $Mg(ClO_4)_2$. Weighed portions of the 2-hydrate were dissolved in a known small volume of H_2O or 2.5 *F* $HClO_4$ at ~15°, and aliquots were taken at once and diluted to volume with preheated amounts of $HClO_4$, HCl, $NaClO_4$ and/or NaCl at 50°; all solutions were aerated with pure N_2 before mixing. Aliquots of the original reaction solutions were diluted and oxidized with Cl_2 within 10 min. after their preparation to check $(IrCl_6^{-3})_0$ spectrophotometrically.

The chloride anation runs were made by dissolving weighed portions of $K_2Ir(OH_2)Cl_5$ in water at 20° and diluting these solutions as described above for the second procedure for the aquation runs.

All reaction solutions, in well-stoppered Pyrex containers, were placed in thermostated baths at 25.05, 35.00 or 50.05° (all ±0.05°) or at 6.0 ± 0.2°. Aliquots of the reaction solutions taken at known times were analyzed spectrophotometrically and/or titrimetrically as described below.

Runs were made in a room illuminated part of the time by fluorescent lights and diffuse daylight; run results did not seem to be affected appreciably by such lighting.

Spectrophotometry.—Optical absorbancies were measured at ~25° with a Cary Model 11 recording spectrophotometer

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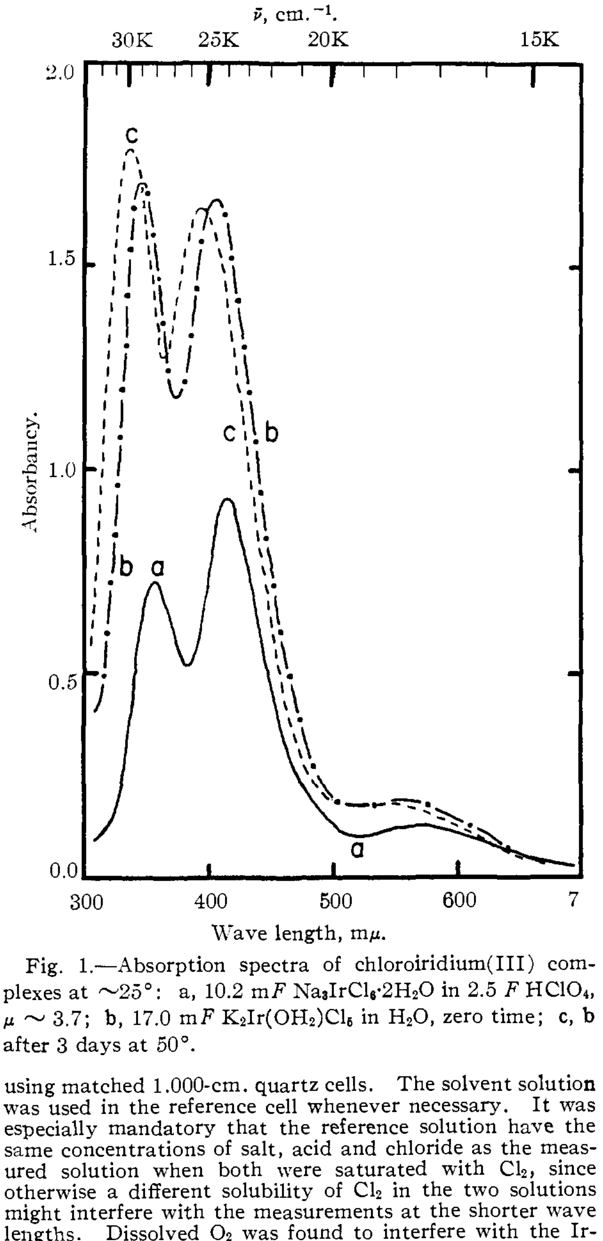

Fig. 1.—Absorption spectra of chloroiridium(III) complexes at ~25°: a, 10.2 mF $Na_3IrCl_6 \cdot 2H_2O$ in 2.5 F $HClO_4$, $\mu \sim 3.7$; b, 17.0 mF $K_2Ir(OH_2)Cl_5$ in H_2O, zero time; c, b after 3 days at 50°.

using matched 1.000-cm. quartz cells. The solvent solution was used in the reference cell whenever necessary. It was especially mandatory that the reference solution have the same concentrations of salt, acid and chloride as the measured solution when both were saturated with Cl_2, since otherwise a different solubility of Cl_2 in the two solutions might interfere with the measurements at the shorter wave lengths. Dissolved O_2 was found to interfere with the Ir(III) spectra, so all Ir(III) solutions run were O_2-free.

For measurements of the molar absorbancy indices of the oxidized species in Cl_2-containing solutions weighed amounts of the complexes were dissolved in water or $HClO_4$ and made up to volume. Aliquots were accurately diluted at once with salt and acid solutions, saturated with Cl_2, to obtain the desired concentrations, and the spectra taken immediately. The spectra of unoxidized $Na_3IrCl_6 \cdot 2H_2O$ and $K_2Ir(OH_2)Cl_5$ were measured immediately after dissolution in O_2-free 2.5 F $HClO_4$ and in O_2-free water, respectively.

One- or five-ml. aliquots of the kinetic-run solutions at the higher complex concentrations were diluted to 25.00 ml. at ~25° with 2.5 F $HClO_4$ saturated with Cl_2 and measured spectrophotometrically. Aliquots from the kinetic runs with $(IrCl_6^{-3})_0 \approx 0.5$ mF were simply cooled to ~0° and saturated with Cl_2 for 5 min. while warming to 25° before the absorbancies were measured.

Titrimetric Procedure.—For determination of the low concentrations of Cl^- released in $IrCl_6^{-3}$ aquation the method of Clarke[25] was used essentially as modified by Smit.[26] However, we found that $IrCl_6^{-3}$ interfered with the titration. Attempts to separate $IrCl_6^{-3}$ from Cl^- on columns of Dowex AG1-X8 (as well as X4 or X10) anion-exchange resin (NO_3^- form) were unsuccessful in the presence of the much higher concentration of ClO_4^- in the aquation-run solutions. Since $IrCl_6^{-2}$ is known[27] to be retained better than $IrCl_6^{-3}$ by anion-exchange resins and since Martinez[4] had shown that $IrCl_6^{-2}$ could be separated from Cl^- by Dowex AG1-X8 resin, we were led to a successful procedure in which the Ir(III) species were oxidized to Ir(IV) with $KMnO_4$ for the separation, as outlined below.

Each 5.00-ml. aliquot of the $(IrCl_6)_0 \approx 10$ mF run solutions was added to 1.0 ml. 0.05 F $Mn(NO_3)_2$ (to avoid oxidation of Cl^-) and the Ir(III) immediately oxidized to Ir(IV) with 1.0 ml. 0.05 F $KMnO_4$ at ~25°. The mixture was passed slowly without suction through a 240-mm. × 9-mm. diam. column of Cl^--free Dowex AG1-X8 anion-exchange resin (50–100 mesh, in NO_3^- form). The free Cl^- was eluted with 25 ml. 0.3 F HNO_3. The eluate was neutralized with solid $NaHCO_3$ and adjusted to pH 3.5 with HNO_3 before the Cl^- was titrated with standardized 0.01 F $Hg(NO_3)_2$. The over-all error depended on the reaction extent, being ~5% and ~1%, respectively, for 10% and 60% release of 1 Cl^- per $IrCl_6^{-3}$. Ir species were spectrophotometrically undetectable in the eluates when <1 Cl^- was released per $IrCl_6^{-3}$.

Results and Discussion

Spectra.—The visible and near-ultraviolet absorption spectra of $IrCl_6^{-3}$, $Ir(OH_2)Cl_5^{-2}$ and their hydrolysis products in aqueous solution (Fig. 1) showed that spectral changes during $IrCl_6^{-3}$ aquation are too small to be useful for following the reaction rate. However, as indicated below, $IrCl_6^{-3}$ and $Ir(OH_2)Cl_5^{-2}$ can be rapidly and quantitatively oxidized in solution by Cl_2 to $IrCl_6^{-2}$ and $Ir(OH_2)Cl_5^-$, respectively. The spectra of these oxidized solutions are given by curves A and B of Fig. 2, for which solutions the optical molar absorbancy indices[28] a show more pronounced differences, especially at 487, 460 and 450 mμ, the wave lengths selected for our experimental studies.

In Cl_2-saturated solutions 0.2–0.5 mF in $Na_2IrCl_6 \cdot 6H_2O$, 0–2.5 F in $HClO_4$ (or HCl) and 0–1.2 F in $NaClO_4$ (or NaCl), average values of a for $IrCl_6^{-2}$ at ~25° were found to be 4050 ± 35, 2080 ± 17 and 2310 ± 40 M^{-1} cm.$^{-1}$ at 487 (max.), 460 (min.) and 450 mμ (max. of $Ir(OH_2)Cl_5^-$), respectively. These values agree with those obtained in Cl_2-free strongly acid solutions of $IrCl_6^{-2}$ by Martinez[4]; other earlier values may be in error because of incomplete knowledge about the water content of the measured salts or because of changes in the salts arising from heating or storage. Values of a for $IrCl_6^{-2}$ rapidly produced by saturating with Cl_2 fresh solutions originally 0.4 mF in $Na_3IrCl_6 \cdot 2H_2O$, 2.5 F in $HClO_4$ and 1.2 F in $NaClO_4$ were the same as above within the errors given.

The previously unreported spectrum of aquopentachloroiridate(IV) anion, $Ir(OH_2)Cl_5^-$, is shown in Fig. 2 (curve B). The a values for $Ir(OH_2)Cl_5^-$ produced by saturating with Cl_2 solutions at ~25° originally 0.3–0.6 mF in $K_2Ir(OH_2)Cl_5$ were found reasonably reproducible only when these solutions were 1–4 F in $HClO_4$ and had an ionic strength $\mu > 2$ (made with $HClO_4$ and/or $NaClO_4$); under these conditions the average a values are 2345 ± 20, 3100 ± 45 and 3320 ± 20 M^{-1} cm.$^{-1}$ at 487,

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460 and 450 mμ, respectively. At lower concentrations of acid and salt the $K_2Ir(OH_2)Cl_5$ solutions on saturation with Cl_2 apparently underwent olation reactions, turning an opalescent brown rather than the normal reddish-orange color. Absorbancies of the above solutions obtained on oxidation of $IrCl_6^{-3}$ and $Ir(OH_2)Cl_5^{-2}$ were constant within experimental error for several hours after the oxidation if loss of Cl_2 was prevented.

Our spectrum for $IrCl_6^{-3}$ (Fig. 1, curve a), obtained on solutions freshly prepared with unheated salts, is in general only in approximate agreement with earlier measurements, which in some cases are only very incompletely reported and in other cases were often obtained under conditions where some oxidation and hydrolysis occurred or where the salts were affected by heating. It is not clear why apparent values of a for $IrCl_6^{-3}$ in solution depend on the temperature and duration of heating of Na_3IrCl_6 (also K^+ salt) prior to dissolution (see Experimental). Partial oxidation to Ir(IV) by air cannot explain the observations since the absorption maxima and minima would be considerably shifted. The extent of any partial hydrolysis to $Ir(OH_2)Cl_5^{-2}$ during drying would have had to be so large that it would have resulted in a detectable weight change (unobserved) and would have given a spectrum on oxidation with Cl_2 different from that observed. Thermal decomposition of $<5\%$ to NaCl and a polymeric iridium(III) chloride may possibly account for the observations.

Our spectrum for $Ir(OH_2)Cl_5^{-2}$ (Fig. 1, curve b) is in reasonable agreement with the a values reported by Jørgensen[18] for the three absorption maxima.

Rate of Aquation of $IrCl_6^{-3}$.—In terms of the optical absorbancies A_0, A and A_∞ (at a given wave length) at time zero t, and at 100% aquation of the first chloro ligand, respectively, the first-order rate equation is

$$\ln[(A_0 - A_\infty)/(A - A_\infty)] = k_1 t \qquad (5)$$

where k_1 is the first-order rate constant for forward reaction 3. Plots of this logarithmic function of the absorbancies at 487 mμ for the $IrCl_6^{-3}$ aquation runs *vs.* t gave straight lines up to 60% aquation for runs with Cl^- initially absent (under which conditions the reverse reaction contributes negligibly). Linear plots also were obtained for the 460- and 450-mμ data, a change in sign of slopes being observed after 70–80% aquation as expected from the spectra of the Cl_2-oxidized aquation products of $Ir(OH_2)Cl_5^{-2}$ (Fig. 2, curve C). Average values of a of Cl_2-oxidized solutions of $K_2Ir(OH_2)Cl_5$ were used to calculate A_∞. Values of k_1, calculated from the slopes of the plots, are given in the last 2 columns of Table I; estimated errors are 5% at 487 mμ and 10% at 460 mμ. Within the 10% error, k_1 values obtained at 450 mμ are the same as at 460 mμ.

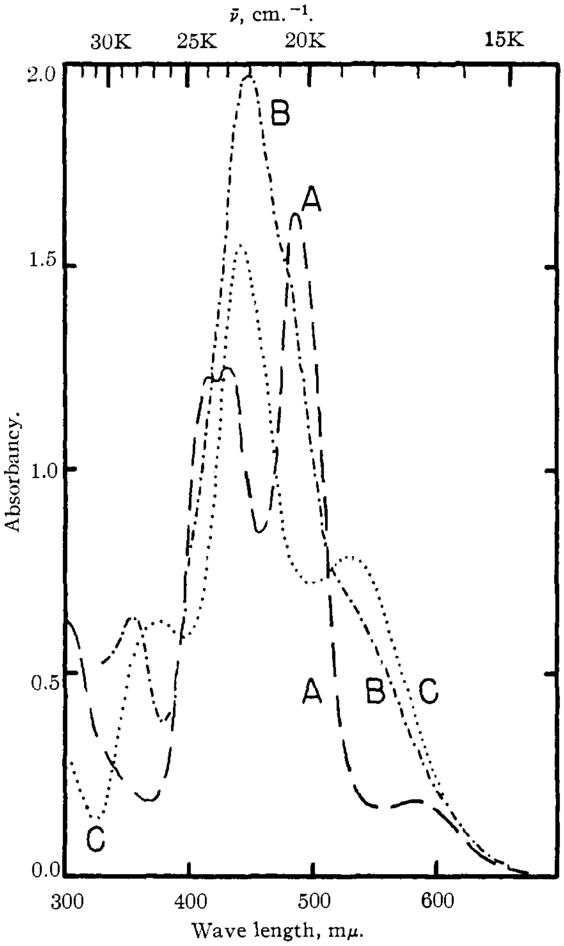

Fig. 2.—Absorption spectra of Fig. 1 solutions at ~25° after dilution and oxidation: A, a oxidized with Cl_2-satd. 2.5 F $HClO_4$ (spectrum of 0.408 mF $IrCl_6^{-2}$); B, b oxidized with Cl_2-satd. 2.5 F $HClO_4$ (spectrum of 0.603 mF $Ir(OH_2)Cl_5^-$); C, c oxidized with Cl_2-satd. 2.5 F $HClO_4$.

Titrimetric determinations of Cl^- released in the aquation of $IrCl_6^{-3}$ permitted calculation of k_1 values, given in column 5 of Table I, for those runs in which Cl^- was initially absent. The molar concentration of $IrCl_6^{-3}$ at time t was taken as $(IrCl_6^{-3}) = (IrCl_6^{-3})_0 - (Cl^-)$. Plots of ln $[(IrCl_6^{-3})_0/(IrCl_6^{-3})]$ *vs.* t gave straight lines up to 60% aquation (runs at 6° and 35° were followed only up to 30% reaction), the slopes of which gave k_1. Errors are estimated as 5–10%. In general, the spectrophotometric and titrimetric k_1 values are in reasonable agreement.

For $IrCl_6^{-3}$ aquation runs in which Cl^- was present initially, the concentration of Cl^- was high enough to remain constant (<0.5% change) during a run, and the anation reaction

$$Ir(OH_2)Cl_5^{-2} + Cl^- \xrightarrow{k_{-1}} IrCl_6^{-3} + H_2O \qquad (6)$$

which contributes can be treated by first-order kinetics. In terms of k_1 and the second-order anation rate constant k_{-1} and the optical absorbancies, the rate equation for the reversible aquation under these conditions becomes

$$\ln[(A_0 - A_e)/(A - A_e)] = [k_1 + k_{-1}(Cl^-)]t \qquad (7)$$

where A_e is the absorbancy at equilibrium. Since $Ir(OH_2)Cl_5^{-2}$ slowly aquates, equilibrium was never attained in the runs, but it was possible for each run of given (Cl^-) to find a value of A_e which would give a straight line in a plot of ln $[(A_0 - A_e)/(A - A_e)]$ *vs.* t (k_1 for the 0.4 M Cl^- run was obtained from equation 5 because of the low concentration of Cl^-). From the slopes of these plots and the equilibrium relation

$$\frac{(Ir(OH_2)Cl_5^{-2})(Cl^-)}{(IrCl_6^{-3})} = K = \frac{k_1}{k_{-1}} = \frac{(Cl^-)(A_0 - A_e)}{(A_0 - A_\infty) - (A_0 - A_e)} = \frac{(Cl^-)(A_0 - A_e)}{(A_e - A_\infty)} \quad (8)$$

values of K, k_1 and k_{-1} at 50.05° (Table II) were calculated from the spectrophotometric data at 487 mμ. The data at 460 and 450 mμ (considered less reliable) gave values of k_1 and k_{-1} about 10–15% different from those for the 487 mμ data and K values <30% different.

The aquation rate constants k_1 at 50° and at constant ionic strength μ are reasonably independent of a 28-fold change in $(IrCl_6^{-3})_0$ (Runs 4,5,8–12), of a 2.5-fold variation in (H^+) (Runs 6,7) and of $(Cl^-)_0$ over the ranges 0–2.2 M at μ = 2.2 (Runs 4,5,8–12) and 1.0–3.4 M at μ = 3.4 (Runs 14,15). Increase of μ from 2.2 to 3.6 decreased k_1 by up to a factor of 2.4 (Runs 4–6,8–15). Ionic strengths are too high to apply any known theory, and there may be specific ionic-interaction effects present. Polynuclear complexes evidently are not significantly involved in the aquation of $IrCl_6^{-3}$.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF $IrCl_6^{-3}$ IN INITIALLY Cl^--FREE SOLUTIONS

Run no.	Temp., °C.	$(IrCl_6^{-3})_0$, mF	$(HClO_4)$, F	μ^a	10^5k_1, sec.$^{-1}$ Cl⁻ detm.	10^5k_1, sec.$^{-1}$ Spectrophotometry 487 mμ	10^5k_1, sec.$^{-1}$ Spectrophotometry 460 mμ
1	6.0	14.95	0.960	2.2	0.023	0.032	0.022
2	25.05	10.54	.960	2.2	0.94	1.04	1.01
3	35.00	11.39	.960	2.2	5.8		
4	50.05	11.46	.960	2.2	40	40	44
5	50.05	0.462	1.008	2.2		36	38
6	50.05	.462	1.012	3.6		16.0	17.0
7	50.05	.460	2.510	3.7		18.5	22.7

[a] Ionic strength adjusted with $NaClO_4$.

TABLE II

EQUILIBRIUM CONSTANTS AND RATE CONSTANTS FOR AQUATION OF $IrCl_6^{-3}$ AND CHLORIDE ANATION OF $Ir(OH_2)Cl_5^{-2}$ IN AQUEOUS Cl^- SOLUTIONS AT 50.05°

Spectrophotometric measurements at 487 mμ

Run no.	(Complex)$_0$, mF	(Cl^-), M	(H^+), M	μ^a	K, M	10^6k_1, sec.$^{-1}$	10^5k_{-1}, M^{-1} sec.$^{-1}$
8	2.190^b	0.401	0.985	2.2		40	
9	2.181^b	.966	0.966	2.2	8.1	42	5.2
10	0.4439^c	.999	1.007	2.2	9.2	37	4.0
11	2.133^b	2.171	0.969	2.2	8.7	39	4.5
12	0.4452^c	2.213	1.008	2.2	8.0	39	4.9
13	10.95^b	2.979	0.975	3.1	4.8	25.3	5.3
14	0.4451^c	1.008	1.008	3.4	3.1	18.2	5.9
15	.4445^c	3.412	1.006	3.4	3.4	17.6	5.2
16	.4973^b	1.205	2.527	3.7	2.16	25.3	11.7
17	.5125^c	1.205	2.527	3.7	2.66	29.1	10.9
18	.4973^b	3.467	2.514	3.7	2.93	23.3	8.0
19	.5110^c	3.457	2.508	3.7	3.2	28.0	8.8

[a] Ionic strength adjusted with $NaClO_4$ and NaCl. [b] $Na_3IrCl_6 \cdot 2H_2O$. [c] $K_2Ir(OH)_2Cl_5$.

The Arrhenius activation energy E_a for the aquation of $IrCl_6^{-3}$ (forward reaction 3), which was obtained from a nearly linear plot of log k_1 *vs.* $1/T$ for the titrimetric values of Table I, is: E_a = 30.4 ± 2.0 kcal., and log PZ = 17.5 ± 1.8 (sec.$^{-1}$). The high pre-exponential factor PZ and the magnitude of the activation energy E_a are not unusual for slow reactions of complex ions in solution.[29]

At 50° the specific rate for aquation of $IrCl_6^{-3}$ is ~400 times that attributed[4] to aquation of $IrCl_6^{-2}$, thus indicating that reactions 2, 3 and 4 can contribute an alternative path for the conversion of $IrCl_6^{-2}$ to $Ir(OH_2)Cl_5^-$ under some circumstances.

Rate of Cl^- Anation of $Ir(OH_2)Cl_5^{-2}$.—Table II presents the values of the second-order anation rate constant k_{-1} found for reaction 6 at 50° as indicated above. For the calculations for anation runs with $Ir(OH_2)Cl_5^{-2}$ as the only iridium species present initially, A_0 and A_∞ were interchanged in equation 8. The rate is shown experimentally to be first-order in $Ir(OH_2)Cl_5^{-2}$ and first-order in Cl^- over the range 1.0–3.4 M Cl^- at μ = 2.2–3.4 (Runs 9–15). At $(H^+) \approx 1$ M k_{-1} is independent of μ over the range 2.2–3.4 (Runs 9–15) within the experimental error. In the range μ = 3.4–3.7, k_{-1} appears to increase with (H^+) (Runs 14–19), but the accuracy of the experiments and the inaccuracy of identifying (H^+) with the total acid formality are such as not to warrant an attempt to deduce the form of a (H^+)-dependent term in the rate law; the effect may be partially an ionic-strength effect. If real, the H^+ catalysis is probably not connected with any acid property of $Ir(OH_2)Cl_5^{-2}$, since our potentiometric titration of 0.94 mF $K_2Ir(OH_2)Cl_5$ (1 F in NaCl) with CO_2- and O_2-free 0.01 F NaOH gave pK_a = 8.8 ± 0.3 at ~25°, in approximate agreement with the value 10.1 obtained by Jørgensen.[18]

Aquation-Anation Equilibrium Constant.—Values of the concentration equilibrium constant K for reaction 3 at 50.05°, obtained as described above, are given in Table II. K is seen to decrease with increasing ionic strength, but the data are not sufficiently accurate and the ionic strengths are too high to justify an extrapolation to infinite dilution. Jørgensen[9] observed spectral changes which he interpreted as a decrease in K for the corresponding $RhCl_6^{-3}$ system in increasing HCl concentration (1–6 F).

Rate of Aquation of $Ir(OH_2)Cl_5^{-2}$.—At 25° and 50° titrimetric determination of Cl^- released in aquation of $IrCl_6^{-3}$ in the range 60–110% aquation of the first chloro ligand allow the first-order aquation rate constant k_2 for the reaction

$$Ir(OH_2)Cl_5^{-2} + H_2O \xrightarrow{k_2} Ir(OH_2)_2Cl_4^- + Cl^- \quad (9)$$

to be estimated as $k_2 \lesssim 0.1k_1$. The method employed requires the separation of iridium species from Cl^-, and above ~100% release of the first chloro ligand iridium-(III) species began to be eluted with Cl^- from the anion-exchange resin and the secondary aquation could not be followed further.

The spectrum of a 2.5 F $HClO_4$ solution of unheated $Na_3IrCl_6 \cdot 2H_2O$ allowed to react under the conditions of Run 7, Table I, for 44 hr. ($IrCl_6^{-3}$ aquation half-time is ~1 hr.) is close in shape

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[29] J. Bjerrum, K. G. Poulsen and I. A. Poulsen, "Reports of the Symposium on Coordination Chemistry," Copenhagen, 1953, p. 51.

and *a* values to curve c, Fig. 1 (hydrolysis of $Ir(OH_2)Cl_5^{-2}$ in water at 50°), suggesting that hydrolysis of $Ir(OH_2)Cl_5^{-2}$ in water at 50° is aquation and not base hydrolysis and further implying that the aquation rates in water and in 2.5 *F* $HClO_4$ are not grossly different. It was not feasible to carry out measurements of spectra on $K_2Ir(OH_2)Cl_5$ in solutions such as those of Tables I and II, owing to the limited solubility of this salt in 1–2.5 *F* $HClO_4$.

[CONTRIBUTION FROM THE WM. A. NOYES LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

Thermodynamic Data for the Association of Phenol with N,N-Dimethylacetamide and N,N-Dimethylmonochloroacetamide

BY MELVIN D. JOESTEN[1] AND RUSSELL S. DRAGO

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Equilibrium constants and enthalpies for the formation of adducts of phenol with N,N-dimethylacetamide, DMA, and N,N-dimethylmonochloroacetamide, DMMCA, are reported. A procedure is indicated for the accurate determination of enthalpies. The heat of formation obtained for the DMA-phenol adduct is compared with enthalpies of formation for the adducts of ICl, I_2, SO_2 and Br_2 with the donor DMA. These acids are a series with widely differing polarizabilities and dipole moments. The effect of these parameters on the enthalpies of adduct formation is discussed qualitatively.

Introduction

In connection with research in this Laboratory concerning the acidity of ICl,[2] I_2,[3] SO_2[2] and Br_2,[2] it was of interest to extend the range of acids studied to include hydrogen bonding types. Phenol was selected because of its ease of handling and convenient ultraviolet absorption.

A large number of equilibrium constants for phenol–base interactions have been summarized by Pimentel and McClellan,[4] but very little reliable enthalpy data are available. In this article a general procedure for obtaining accurate enthalpy data is outlined. The results obtained with phenol as the acid are compared with the enthalpies obtained for some halogen acids and sulfur dioxide.

Experimental

Materials.—Fisher Spectranalyzed carbon tetrachloride was used without further purification. Purification of DMA has been described previously.[5] DMMCA, $ClCH_2CON(CH_3)_2$, was prepared from the corresponding chloroacetylchloride. The amide was fractionally distilled at about 2 mm. pressure, and the fraction boiling at 85° was collected.

Anal. Calcd. for $ClCH_2CON(CH_3)_2$: C, 39.52; H, 6.63; N, 11.52. Found: C, 39.62; H, 6.68; N, 11.47.

Baker and Adamson Reagent Grade phenol was distilled at atmospheric pressure. The fraction boiling at 182° was collected.

Apparatus.—Preliminary spectra were recorded with a Cary model 14M spectrophotometer. After selection of an appropriate wave length, a Beckman D.U. spectrophotometer equipped with a temperature controlled, forced air, heating system was employed for all measurements. The temperature of the solution was measured directly with a thermistor located in a well in the sample cell.

Sample Preparation.—Phenol and amide master solutions were prepared by weighing these materials in volumetric flasks and diluting with carbon tetrachloride. The sample solutions were prepared from aliquots of these stock solutions. Concentrations were corrected for volume changes at various temperatures. To avoid formation of polymeric species, phenol concentrations of $4 \times 10^{-3}M$ or less were used.

Procedure.—The following equation was derived[6] and employed for equilibrium constant calculations

$$K^{-1} = \frac{A - A^0 - A_D}{\epsilon_C - \epsilon_A - \epsilon_D} - C_A - C_D + \frac{C_A C_D(\epsilon_C - \epsilon_A - \epsilon_D)}{A - A^0 - A_D} \quad (1)$$

A, absorbance of system at a given wave length; A^0, absorbance due to initial phenol concentration; A_D, absorbance due to initial amide concentration; ϵ_c, molar absorptivity of complex; ϵ_A, molar absorptivity of phenol; ϵ_D, molar absorptivity of amide; C_A, initial concentration of phenol; C_D, initial concentration of amide. Its derivation is similar to that reported[7] for the case where A_D and ϵ_D are zero.

The quantity A–A^0 is obtained directly by measuring the absorbance difference of a carbon tetrachloride solution of phenol in the reference cell and a phenol–amide solution of similar total phenol concentration in the sample cell. The entire spectrum was traced in the ultraviolet region in order to find the optimum wave length for study, *i.e.*, the region of largest absorbance change. The phenol adduct absorbs in the same region as free phenol but the adduct has a higher molar absorptivity. Both donor systems exhibit the largest difference in absorbance at 284 and 277 mμ. Equilibrium constant and enthalpy measurements were made at 284, 277 and 288 mμ. Agreement in the values measured at all three wave lengths is obtained.

Two types of experiments were performed to obtain the thermodynamic data. In one, referred to hereafter as an equilibrium constant determination, the absorbance of each of several solutions was measured at constant temperature. The equilibrium constants and the values for $\epsilon_C - \epsilon_A - \epsilon_D$ were calculated from data obtained at several temperatures by use of equation 1.[7] In the other procedure, referred to as an enthalpy determination, very precise enthalpy results are obtained by measuring the absorbance change of a single solution as a function of temperature. The values for $\epsilon_C - \epsilon_A - \epsilon_D$ obtained at various temperatures from the equilibrium constant experiment are used in equation 1 for the calculation of the values of K in the enthalpy experiment.

The quantities A_D and ϵ_D were determined for the free amide at various temperatures.

In employing equation 1, one subtracts A_D from the $A - A^0$ readings and obtains the quantity $\epsilon_C - \epsilon_A - \epsilon_D$ from the K^{-1} *vs.* ϵ plot.[7]

Table I contains data on the temperature dependence of the molar absorptivities of DMMCA and phenol.

A negligible amount of error is introduced in the enthalpy calculations by neglecting variation in A_D with temperature at 284 and 288 mμ. This change cannot be neglected at 276 mμ.

The temperature dependence of the term $\epsilon_C - \epsilon_A - \epsilon_D$ was determined from equilibrium constant determinations at

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