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Kinetics of Aquation of Hexachloroosmate(IV) and Chloride Anation of Aquopentachloroosmate(IV) Anions[1]

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The kinetics of the reactions $OsCl_6^{-2} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Os(OH_2)Cl_5^- + Cl^-$ have been investigated in HCl medium at 80°; the forward reaction has also been studied at 70–89° in HNO_3 medium, in which the aquation product and secondary products are rapidly oxidized to OsO_4 and Cl^-. In 0.00001–0.1 F HNO_3 (μ = 0.5–1.32, $NaNO_3$), and by deduction in HCl of the same acidity, $k_1 = 3.5 \times 10^{-6}$ sec.$^{-1}$ at 79.53° in the dark; $E_a = 33.1 \pm 0.6$ kcal., log $pZ = 15.1 \pm 0.4$ (sec.$^{-1}$), $\Delta H^{\circ *}_{298} = 32.5 \pm 0.6$ kcal., $\Delta S^{\circ *}_{298} = 8 \pm 2$ cal. deg.$^{-1}$, k_1 (calcd.) = $(6 \pm 1) \times 10^{-10}$ sec.$^{-1}$ at 25°. In 0.5–1.32 F HNO_3 (μ = 1.32, $NaNO_3$) at 80° the rate of disappearance of $OsCl_6^{-2}$ is up to 30% greater than for 0.00001–0.1 F H^+, apparently due to a contribution from oxidation of $OsCl_6^{-2}$ to OsO_4 and Cl^-. In 0.01–1.32 F HCl (μ = 1.32, NaCl) at 80°, the previously uncharacterized $Os(OH_2)Cl_5^-$ is the only product observed at short reaction times; the rate of loss of $OsCl_6^{-2}$ in 1.32 F H^+ (where $k = 4.17 \times 10^{-6}$ sec.$^{-1}$, close to k_1 in 0.00001–0.1 F HNO_3, μ = 1.32, at 80°) is *ca.* 14 times that in 0.01 F H^+. Rate runs made in 0.016 F HCl with added low concentrations of different oxidants give k values approaching or nearly equal to k_1 for 0.00001–0.1 F HNO_3; the abnormally high rates of $OsCl_6^{-2}$ loss in HCl at low acidities may arise from reduction by Cl^- of very small amounts of $OsCl_6^{-2}$ to one or more hydrolytically more labile complexes. Chloride anation of $Os(OH_2)Cl_5^-$ was studied at 79.53° in 2.49–3.80 F Cl^-, 2.46–3.80 F H^+ (μ = (Cl^-), KCl). An exact first-order dependence on (Cl^-) was not observed, 10^5k_{-1} varying from 1.01 to 1.97 M^{-1} sec.$^{-1}$; in 3.3–3.8 F HCl $k_{-1} \approx 2 \times 10^{-5}$ M^{-1} sec.$^{-1}$. The visible and near-ultraviolet absorption spectrum of $Os(OH_2)Cl_5^-$ is reported. Compounds described in the literature as "pentachlorohydroxy osmate(IV)" salts, $M_2[Os(OH)Cl_5]$, are very probably binuclear complexes, $M_4[Cl_5OsOOsCl_5]\cdot H_2O$.

The hydrolysis of hexachloroosmate(IV) anion apparently has been only superficially investigated previously. The visible absorption spectrum of this complex in 1.32 or 0.1 F HNO_3 was observed[2] not to change in 1 week at 50°, but to alter greatly after 56 days in 0.1 F HNO_3 at 50°, less than 5% exchange with radiochloride ion being found under those conditions. The rate of isotopic exchange between hexachloroosmate(IV) ion labeled with radiochlorine and chloride ion has been measured.[3] There seems to be no published work on chloride anation[4] of the aquopentachloroosmate(IV) anion, nor even on the characterization of this species.

We report here evidence for the aquopentachloroosmate(IV) anion, together with a study of the kinetics of the reversible reactions

$$OsCl_6^{-2} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Os(OH_2)Cl_5^- + Cl^- \quad (1)$$

The investigation was greatly impeded by lack of substances suitable for control of acid concentration and ionic strength. Aquation could not be studied in perchloric acid medium, inasmuch as temperatures of *ca.* 80°, required for adequate aquation rates, result in oxidation of hexachloroosmate(IV) ion by perchloric acid if (ClO_4^-) $\gtrsim$ 0.5 F and (H^+) $\gtrsim$ 0.05 F. In sulfuric acid and trifluoroacetic acid media, as well as perchloric acid if (ClO_4^-) = 0.5 F and (H^+) $\lesssim$ 0.05 F, black precipitates form before enough primary aquation of hexachloroosmate(IV) ion has occurred to allow following the aquation rate. Nitric acid medium is satisfactory for following the rate of disappearance of hexachloroosmate(IV) ion, but all hydrolysis products are rapidly oxidized by the nitric acid to osmium(VIII) oxide and chloride ion, and the hydrolysis products cannot be examined in this medium. Hydrochloric acid medium is suitable for following both hexachloroosmate(IV) disappearance and examining the hydrolysis products, but is complicated by competition from the back reaction, by formation of black precipitates and other secondary products at early reaction times, and apparently, especially at low hydrogen ion concentrations, by heterogeneous catalysis or from low concentrations of one or more hydrolytically more labile osmium complexes arising from possible reduction of hexachloroosmate(IV) ion by chloride ion at the elevated temperatures involved. Consequently, we report below kinetic studies made only in nitrate and chloride media.

Observations on the nature of the alleged ("NH_4)$_2$-$OsCl_5OH$" are presented.

Experimental

Ammonium Hexachloroosmate(IV).—This compound was made by the method of Dwyer and Hogarth[5,6] and recrystallized from 3 F HCl at 40° by adding 20% NH_4Cl dropwise, then cooling in ice. The deep red crystals were washed with 80% ethanol, absolute ethanol, and anhydrous ether; yield 90%. *Anal.* Calcd. for $(NH_4)_2OsCl_6$: Os, 43.4; Cl, 48.5. Found: Os, 43.7; Cl, 47.9. The absorption spectra of the purified products in 2.5 F

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

(2) L. L. Larson and C. S. Garner, *J. Am. Chem. Soc.*, **76**, 2180 (1954).

(3) R. Dreyer and I. Dreyer, *Z. Chem.*, **4**, 106 (1964). This paper came to our attention after our original manuscript was submitted for publication. The exchange was measured only in 8.8 F HCl at 80–100°, with ($OsCl_6^{-2}$) = 3 mF, and the relative contributions to the exchange of hydrolysis and direct biomolecular exchange are not known. A factor of 6 was omitted in front of each (A) in their McKay equation relating F and R, but apparently their rate plot was unaffected.

(4) Anation is the replacement of ligand water in a complex by an anion.

(5) F. P. Dwyer and J. W. Hogarth, *J. Proc. Roy. Soc. N. S. Wales*, **84**, 194 (1951).

(6) F. P. Dwyer and J. W. Hogarth, *Inorg. Syn.*, **5**, 206 (1957).

$HClO_4$ at 25° (see Figure 1) agreed well with the spectrum reported[2] for K_2OsCl_6 in 1.32 *F* HNO_3–0.06 *F* NaCl (we found 2–5% lower molar absorbancy indices at absorption peaks and minima except for the 404-mμ minimum which was 2% greater) and with the spectrum of $OsCl_6^{-2}$ (cation and medium not stated) reported by Jørgensen.[7]

Aquopentachloroosmate(IV) Anion.—This previously uncharacterized complex was obtained in solution only, by chromatographic separation from $OsCl_6^{-2}$ aquation mixtures. *Ca.* 25–250 μfwt. of $(NH_4)_2OsCl_6$ was aquated in 1.32 *F* HCl at 80°, usually for 23–46 hr. (*ca.* 0.5–1 half-time), then put on a 1-cm. diameter × 10-cm. Cl^- or HSO_4^- Dowex AG 1-X8 (100–200 mesh) anion-exchange column at *ca.* 25°. Secondary reaction products were eluted with 500–700 ml. of 6 *F* HCl (Cl^- resin) or *ca.* 700 ml. of 11 *F* H_2SO_4 (HSO_4^- resin), followed by 0.5 *F* $HClO_4$; the $HClO_4$ effluents were discarded until the ratio of optical absorbancies at 344 mμ ($Os(OH_2)Cl_5^-$ absorption peak) and 380 mμ (region of absorption peaks of secondary products) became *ca.* 2.2 (ratio of molar absorbancy indices of $Os(OH_2)Cl_5^-$ at 344 and 380 mμ). Then 150 ml. of 0.5 *F* $HClO_4$ or 350 ml. of 0.75 *F* HCl–0.25 *F* $HClO_4$ was used to elute $Os(OH_2)Cl_5^-$ (more eluent causes contamination with $OsCl_6^{-2}$). The resulting solutions were usually *ca.* 0.01–0.2 m*F* in $Os(OH_2)Cl_5^-$. Flow rates of *ca.* 1.5 ml./min. resulted in long elution times which could be greatly shortened when little secondary product was present by use of ClO_4^- Dowex AG 1-X8 columns (unsuitable for separation of secondary products) with *ca.* 150 ml. of 0.85 *F* HCl–0.15 *F* $HClO_4$ eluent.

When Cl/Os atom ratios were to be determined on the $Os(OH_2)Cl_5^-$ effluents only the HSO_4^- resin and Cl^--free eluting agents were used.

Chromatography of Secondary Reaction Products and of $OsCl_6^{-2}$.—Attempts to separate cleanly by ion-exchange techniques all secondary products (which begin to appear after *ca.* 5 hr.) in the reaction of $OsCl_6^{-2}$ in 1.32 *F* HCl at 80° have failed. Dowex AG 1-X8 anion-exchange resin (100–200 or 50–100 mesh) was tried in Cl^-, ClO_4^-, HSO_4^-, and $F_3CCO_2^-$ forms (NO_3^- form oxidizes all reaction products), usually with the corresponding acid as eluting agent. Columns (5–30 cm.) were operated at *ca.* 25° ($F_3CCO_2^-$ columns were operated at 0° to reduce the amount of a dark band at the column top).

The first secondary product to appear in the hydrolysis mixtures could be chromatographed out in reasonably pure condition by first eluting two or more other secondary products from HSO_4^- Dowex AG 1-X8 resin with 250 ml. of 0.4 *F* H_2SO_4, then eluting the first secondary product with 350 ml. of 1.6–1.8 *F* H_2SO_4. This species was found to have a Cl/Os atom ratio of 3.81, in reasonable agreement with the formula $Os(OH_2)_2Cl_4$. Since either geometrical isomer of this species is neutral and should have been eluted more readily, the complex may be $Os(OH_2)_2Cl_4^-$ (reduction in solution or by the resin), $(H_2O)Cl_4OsOOsCl_4(OH_2)^{-4}$, or $(H_2O)Cl_4OsOOsCl_4(OH_2)^{-2}$. The spectral evidence favors the latter in that the species has a narrow absorption band at 377 mμ with a_M = 11,200 M^{-1} cm.$^{-1}$ (this band remains unchanged if the species is instead eluted with 1.5–1.8 *F* HCl off Cl^- Dowex AG 1-X8), remarkably similar to the narrow band of $(NH_4)_4[Cl_5OsOOsCl_5] \cdot H_2O$ (see next section) at 397 mμ with a_M = 10,900 M^{-1} cm.$^{-1}$.

Unreacted $OsCl_6^{-2}$ is more tightly bound to the resin than any of the observed reaction products. At 25° *ca.* 80% and at 40° 95–99% of the $OsCl_6^{-2}$ can be eluted with 250–400 ml. of 1–4 *F* $HClO_4$; quantitative separation from $Os(OH_2)Cl_5^-$ was not achieved.

Ammonium Decachloro-μ-oxodiosmate(IV) 1-Hydrate.—Substances described as alkali metal and ammonium hydroxopentachloroosmate(IV) compounds, $M_2[Os(OH)Cl_5]$, have been reported.[5,8] Dwyer and Hogarth[5] stated their "$(NH_4)_2[Os(OH)Cl_5]$" could be boiled with concentrated HCl in the presence of NH_4Cl without formation of $(NH_4)_2OsCl_6$. This is not the be-

(7) C. K. Jørgensen, *Mol. Phys.*, **2**, 309 (1959).

(8) F. Krauss and D. Wilken, *Z. anorg. allgem. Chem.*, **137**, 360 (1924).

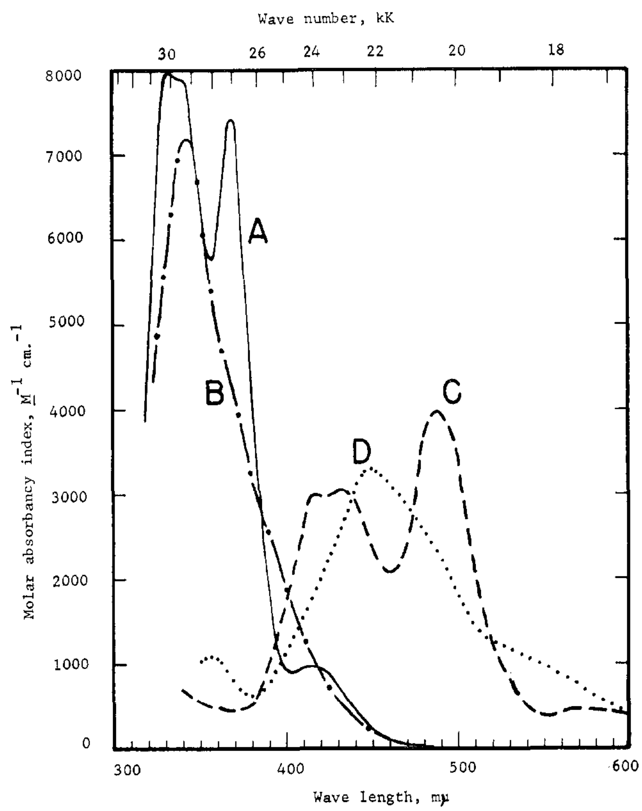

Figure 1.—Absorption spectra of osmium(IV) and iridium(IV) complexes at 25°: A, $OsCl_6^{-2}$ in 2.5 *F* $HClO_4$ or 3.8 *F* HCl; B, $Os(OH_2)Cl_5^-$ in 2.5 *F* $HClO_4$; C, $IrCl_6^{-2}$ in Cl_2-saturated 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$ (ref. 15); D, $Ir(OH_2)Cl_5^-$ in Cl_2-saturated 2.5 *F* $HClO_4$–1.2 *F* $NaClO_4$ (ref. 15). The molar absorbancy index a_M (also called the molar extinction coefficient ε) is related to the absorbancy *A* by $A = \log (I_0/I) = a_M cd$.

havior expected for a salt of $Os(OH)Cl_5^{-2}$. Since $Os(OH)Cl_5^{-2}$ would be of interest in our hydrolysis study of $OsCl_6^{-2}$, we repeated the synthesis given by Dwyer and Hogarth. The dark greenish brown product was recrystallized from the minimum volume of 3 *F* HCl at 40° by adding solid NH_4Cl, cooling in ice, and washing with 90% ethanol, absolute ethanol, and ether. The blue-black crystals were dried overnight under vacuum at 75°; yield 13%. *Anal.* Calcd. for $(NH_4)_4[Cl_5OsOOsCl_5] \cdot H_2O$ or "$(NH_4)_2OsCl_5OH$": Os, 45.2; Cl 42.2; N, 6.66. Found: Os, 46.1; Cl, 43.4; N, 6.79. This substance gave the same visible absorption spectra in 2.5 *F* $HClO_4$ and in 2.5 *F* $LiClO_4$ (absorption peak at 397 mμ, a_M = 10,900 M^{-1} cm.$^{-1}$; shoulder at 330 mμ), and a similar spectrum in 2.5 *F* $LiClO_4$ made 4 m*F* in NaOH (peak at 399 mμ, a_M = 10,300 M^{-1} cm.$^{-1}$; shoulder at 330 mμ). These spectra are very different from that of $Os(OH_2)Cl_5^-$ in 2.5 *F* $HClO_4$ (Figure 1). Hence the Dwyer–Hogarth compound does not contain the $Os(OH)Cl_5^{-2}$ ion, since it should rapidly protonate in 2.5 *F* $HClO_4$ to $Os(OH_2)Cl_5^-$. The compound is almost certainly the binuclear complex $(NH_4)_4[Cl_5OsOOsCl_5] \cdot H_2O$. Analogous compounds of Ru(IV), $M_4[Cl_5RuORuCl_5] \cdot H_2O$, are known in the solid state[9] and the complex anion has been shown to exist in aqueous solution.[10] One H_2O is lost per two Ru at elevated temperatures (300° for the K^+ salt)[11]; we found no loss of H_2O for the Dwyer–Hogarth compound at 75° *in vacuo* overnight.

Other Chemicals.—All other chemicals were reagent grade or C.P. The water was doubly distilled, then passed through a

(9) A. McL. Mathieson, D. P. Mellor, and N. C. Stephenson, *Acta Cryst.* **5**, 185 (1952).

(10) N. K. Pshenitsyn and N. A. Ezerskaya, *Zh. Neorgan. Khim.*, **5**, 1068 (1960), through *Chem. Abstr.*, **55**, 3267*h* (1961).

(11) R. Charonnat, *Ann. Chim. Phys.*, **16**, 5 (1931).

mixed-bed cation–anion resin and monitored for purity by electrical conductivity.

Chemical Analyses.—Weighed samples of $(NH_4)_2OsCl_6$ (vacuum dried at 95° for 3 hr.) were analyzed by reducing with H_2 at 500° for 3 hr. in a quartz combustion tube equipped with traps to catch the HCl and NH_4Cl formed, titrating this Cl^- with $AgNO_3$ solution, and weighing the Os metal residue (cooled and weighed in O_2-free N_2 to prevent oxidation).

The Dwyer–Hogarth compound, "$(NH_4)_2OsCl_5OH$," was analyzed for Os by the above method. The Cl analysis was performed by decomposing the complex in 0.1 F NaOH at 80° for 1.5 hr., then adding a few crystals of $Al_2(SO_4)_3$ to help coagulate the precipitate, centrifuging it out, and titrating the combined centrifugate and washings for Cl^- by the method of Clarke.[12]

Solutions of $Os(OH_2)Cl_5^-$ or the 377-mμ secondary product, and certain reaction solutions, were analyzed for Os by either of two methods, with closely agreeing results. In one, the solution was first treated with saturated KCl solution in 10% excess at 0° if ClO_4^- was present and the $KClO_4$ filtered off to avoid up to 10% loss of Os (probably as volatile OsO_4), then to 5 ml. of this solution were added 10 ml. of 2.5 F LiCl and 3 ml. of 12 F HCl and the solution was evaporated at 80° to one-fifth of its volume (*ca.* 1 hr.) to anate $Os(OH_2)Cl_5^-$ or 377-mμ product quantitatively to $OsCl_6^{-2}$, which was determined spectrophotometrically at 370 mμ. The other method is a modification of several related methods.[13–15] Enough 12 F HCl was added to 25.0 ml. of sample solution to make it 6 F in HCl. To this were added 1 ml. of 1% $SnCl_2$ in 2.4 F HCl and 2 ml of 10% thiourea in water. The mixture was heated to 75 ± 2° for 30 min., then let stand 48 hr. at room temperature to develop the red complex,[16] $Os(NH_2CSNH_2)_6^{+3}$. The optical absorbancy was compared at 480 mμ with that of solution prepared from a known amount of $(NH_4)_2OsCl_6$ treated identically. The method was tested as low as 0.5 μF in complex (absorbancy of 0.23 in a 10-cm. cell).

The 377-mμ product and $Os(OH_2)Cl_5^-$ isolated in Cl^--free column effluents were analyzed for Cl as follows. The effluents were made 0.05 F in NaOH, heated to near boiling for 1.5 hr., cooled, and then made up to volume. Aliquots (20.00 ml.) were added to 100.0-ml. portions of an acetone-detergent solution[17] (3 ml. of 16 F HNO_3, 92 ml. of water, and 5 ml. of Union Carbide Tergitol Nonionic NPX, mixed well, then stirred into 400 ml. of reagent grade acetone). These solutions were titrated for Cl^- (*ca.* 3 μequiv.) with 1 mF $AgNO_3$, using silver and saturated calomel electrodes (the latter connected *via* a KNO_3 salt bridge) with a Radiometer Model PHM-4c pH meter as potentiometer. The end point e.m.f. was determined with known Cl^- samples in solutions of the same ionic strength and with the same amounts of all reagents used to correct for Cl^- in them.

Kinetic Aquation Runs.—Weighed amounts of $(NH_4)_2OsCl_6$ were dissolved in the appropriate medium and made up to volume, and 3-ml. portions were sealed by torch in Pyrex ampoules, which were placed in a thermostated bath. Ampoules were removed at known times, quenched in ice, and the contents then analyzed as follows.

The reaction in NO_3^- medium was followed by determining spectrophotometrically at 370 mμ the concentration of unreacted $OsCl_6^{-2}$, since all reaction products observed in HCl medium are oxidized in HNO_3 medium to OsO_4 and Cl^- rapidly at 80° and within 3 hr. at 25°, whereas little if any $OsCl_6^{-2}$ is oxidized at 80° (except possibly at $(HNO_3) > 0.1$ F) and none at 25° in the times involved. At the concentrations involved OsO_4 absorbs negligibly at 370 mμ. In some runs Cl^- release was followed by putting run samples on 1-cm. diameter × 4-cm. NO_3^- Dowex AG 1-X8 (50–100 mesh) columns prefilled with 0.2 F HNO_3; the Cl^- was eluted quantitatively with 0.30 F HNO_3 to a total collected volume of 50 ml. and determined potentiometrically. Rate constants k were evaluated graphically by the equation $k = -2.30\ \Delta \log [6(OsCl_6^{-2})_0 - (Cl^-)]/\Delta t$ or $k = -2.30\ \Delta (\log A)/\Delta t$, where A is the absorbancy at 370 mμ at time t.

In Cl^- medium $OsCl_6^{-2}$ disappearance was followed spectrophotometrically after oxidation of reaction products to OsO_4 by HNO_3; 1-ml. aliquots of reaction mixture were diluted to 50 ml. with 2.5 F $HClO_4$–0.1 F $NaNO_3$. After at least 3 hr. at 25° the absorbancy was measured at 370 mμ.

Kinetic Anation Runs.—After synthesis and chromatographic isolation of $Os(OH_2)Cl_5^-$ off a Cl^- exchange-resin column with 0.75 F HCl–0.25 F $HClO_4$, ClO_4^- was removed by adding KCl, cooling to 0°, and filtering off the $KClO_4$. Enough 12 F HCl, and in some cases KCl also, was added to give the desired anation reaction solution. The total formality of Os, (ΣOs), and the initial concentration of free Cl^- were determined by the thiourea method and Mohr method, respectively. The initial concentration of $Os(OH_2)Cl_5^-$ was taken as $(\Sigma Os) - (OsCl_6^{-2})_0$; $(OsCl_6^{-2})_0$ was 4 to 15% of (ΣOs) and was obtained from the known molar absorbancy index of $OsCl_6^{-2}$ at 370 mμ in the medium involved and the absorbancy at 370 mμ of a zero-time run aliquot to which NO_3^- was added at 25° to destroy all complexes except $OsCl_6^{-2}$. Run samples (40 ml.) were sealed by torch in Pyrex ampoules, allowed to react in a thermostat bath, quenched, and the extent of anation followed by two independent methods.

In one method the run samples were allowed to stand at least 3 hr. at 25° after being made 0.1 F in NO_3^- to destroy all complexes except $OsCl_6^{-2}$. Rate constants k were obtained graphically from the absorbancies at 370 mμ by use of $k = -2.30\Delta [(\Sigma Os) - (OsCl_6^{-2})]/\Delta t$.

In the second method the absorption spectra of reaction mixture aliquots taken at known reaction times were scanned at 25° from 325 to 500 mμ to search for isosbestic points and to permit calculation of rate constants from 2.30 times the slopes of plots of $-\log (A_\infty - A)$ *vs.* t at 370 mμ; A_∞ is the theoretical absorbancy if the anation went 100% to $OsCl_6^{-2}$, obtained from (ΣOs).

In all runs, aquation and anation, light was routinely excluded from the samples during their reaction.

Spectrophotometry.—Absorption spectra of kinetic anation run solutions and of $OsCl_6^{-2}$, $Os(OH_2)Cl_5^-$, and chromatographically separated reaction-product fractions were scanned at 25° with a Cary Model 11 recording spectrophotometer, using matched 10.00-cm. quartz cells. Solutions identical with the sample solution except without Os complexes were used in the reference cell. In chemical analyses and kinetic aquation runs absorbancies were read on a Beckman DU spectrophotometer.

Results

Primary Product of Reaction of $OsCl_6^{-2}$ in 1.32 F HCl at 80°.—Chromatography of these reaction mixtures on a ClO_4^--resin column at reaction times up to *ca.* one-twelfth the aquation half-time revealed only a single reaction product, the near-ultraviolet and visible absorption spectrum of which is characterized by a single absorption band at 344 mμ. The spectrum was unchanged when this substance was isolated at longer reaction times with HSO_4^- or Cl^- anion-exchange resin.

The Cl/Os atom ratio of this product isolated from mixtures which had reacted for *ca.* 0.5 and 1 half-time was 5.02, 4.80, and 4.81, in reasonable agreement with the theoretical value for $Os(OH)_2Cl_5^-$, the previously uncharacterized expected primary aquation product.

The chromatographic behavior of this species also supports its characterization as $Os(OH_2)Cl_5^-$; the order of elution off Dowex AG 1-X8 columns is secondary products, primary aquation product, then $OsCl_6^{-2}$,

(12) F. E. Clarke, *Anal. Chem.*, **22**, 553 (1950).
(13) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, D. Van Nostrand Co., New York, N. Y., 1949, p. 536.
(14) W. R. Schneller and A. R. Powell, "The Analysis of Minerals and Ores of the Rarer Elements," Hafner Publishing Company, New York, N. Y., 1955, p. 344.
(15) S. T. Payne, *Analyst*, **85**, 698 (1960).
(16) R. Sauerbrunn and E. B. Sandell, *J. Am. Chem. Soc.*, **75**, 3554 (1953).
(17) V. J. Shiner, Jr., and M. L. Smith, *Anal. Chem.*, **28**, 1043 (1956).

the same order found[18,19] in chromatography of $IrCl_6^{-3}$ aquation mixtures after oxidation to Ir(IV), namely, secondary products, $Ir(OH_2)Cl_5^-$, then $IrCl_6^{-2}$. Moreover, the concentration and volumes of eluting agents required to elute $Ir(OH_2)Cl_5^-$ and the presumed $Os(OH_2)Cl_5^-$ are very similar: 100 ml. of 0.5 *F* $NaNO_3$–0.001 *F* $HClO_4$ for the former and 150 ml. of 0.5 *F* $HClO_4$ for the latter.

Figure 1 shows that the absorption spectra of $OsCl_6^{-2}$ and $IrCl_6^{-2}$ each exhibit four bands (two of which overlap strongly), the $OsCl_6^{-2}$ bands being more intense and displaced strongly toward lower wave lengths. The species we characterize as $Os(OH_2)Cl_5^-$ and the known $Ir(OH_2)Cl_5^-$ have spectra with one main band, plus a second band appearing as a shoulder on the high wave length side of the main peak, again with the Os bands more intense and displaced toward lower wave lengths (the $Os(OH_2)Cl_5^-$ counterpart of the low-intensity band of $Ir(OH_2)Cl_5^-$ at 357 mμ would be expected to lie below the lowest wave length to which it was convenient to scan the $Os(OH_2)Cl_5^-$ spectrum).

Attempts to obtain the spectrum of $Os(OH)Cl_5^{-2}$ by basifying HCl solutions of $Os(OH_2)Cl_5^-$ led to rapid formation of dark precipitates, even at pH 5, perhaps due to olation and/or reduction. We were able to take the spectrum of $Os(OH_2)Cl_5^-$ in HCl solution at pH 2.11 (no change from the spectrum in 2.5 *F* $HClO_4$), add solid $NaHCO_3$ to give a pH of 3.65 (the 344-mμ band shifted to 330 mμ, without significant change in spectrum shape above 330 mμ), wait 15 min. (no spectral change except a barely noticeable increase in absorption background at 460–500 mμ), then add $HClO_4$ to return the pH to 2.11 with an overall dilution of only 0.2% (essentially no change from the original spectrum except a 2% loss in intensity of the 344-mμ band). Whatever this spectral change with pH represents it is rapid and essentially reversible.

Rate of Aquation of $OsCl_6^{-2}$.—In HNO_3 of constant ionic strength and NO_3^- concentration, both 1.32 *F*, disappearance of $OsCl_6^{-2}$ at 80° gave good first-order rate plots as far as the reaction was followed (13–16% in two runs, 20–57% in all others), and no reaction products other than OsO_4 and Cl^- were detected. Table I shows the effect of H^+ concentration on the first-order rate constant k_N.

Since we have shown that $Os(OH_2)Cl_5^-$ and secondary reaction products of $OsCl_6^{-2}$ in HCl media are rapidly oxidized by NO_3^- to OsO_4 at 80°, k_N could be for a rate-controlling hydrolysis of $OsCl_6^{-2}$ or for oxidation of $OsCl_6^{-2}$ to OsO_4, or some of each. However, the rate of oxidation by NO_3^- would be expected to depend strongly on the H^+ concentration over the 10^5-fold range shown in Table I, whereas $OsCl_6^{-2}$ aquation should be approximately acid independent, and a contribution from base hydrolysis of $OsCl_6^{-2}$ would give rate constants increasing with increasing pH. Within experimental error (*ca.* 3% standard error) k_N is constant from pH 1 to >5, suggesting that the reaction is aquation (forward reaction 1, Introduction) over this range. The greater values of k_N above 0.1 *F* H^+ may be attributed to a contribution from oxidation of $OsCl_6^{-2}$ to OsO_4, increasing from negligible oxidation at 0.1 *F* H^+ to 24% at 1.32 *F* H^+. Thermodynamically, and probably kinetically, NO_3^- becomes a better oxidant at higher H^+ concentration. Parenthetically, we note that in 0.01 *F* NaOH (μ = 1.32, $NaNO_3$) essentially all the $OsCl_6^{-2}$ reacts within 1 hr. at 80° to form a black precipitate.

TABLE I

ACID DEPENDENCE OF LOSS OF $OsCl_6^{-2}$ IN HNO_3 AT 79.53 ± 0.03°, μ = 1.32 ($NaNO_3$)

(HNO_3), *F*	($OsCl_6^{-2}$)$_0$, m*F*	$10^6 k_N$, sec.$^{-1}$
1.32	2.82	4.63[a]
1.32	5.31	4.56[a]
0.75	4.69	4.18
0.50	4.69	4.20
0.10	4.80	3.41
0.10[b]	3.86	3.58
0.010	4.76	3.49
0.0010	4.44	3.47
0.000010	4.52	3.48
None added	4.70	3.47

[a] Same value found spectrophotometrically and by titration of Cl^- released; all other values found by spectrophotometric method. [b] μ = 0.50.

As a test of this aquation hypothesis we may examine the rate of $OsCl_6^{-2}$ disappearance in HCl medium of the same ionic strength. In HCl medium we cannot measure released Cl^-, nor can we separate quantitatively from the reaction mixtures either $Os(OH_2)Cl_5^-$ or $OsCl_6^{-2}$ to follow as a function of time. Moreover, black precipitates[20] (none in 1.32 *F* HCl) and other secondary products form at such early reaction times that one cannot determine rates from the change in absorption spectrum of the reaction solution before precipitation or preceding opalescence sets in, or before secondary products appear. Isosbestic points are not observed in the spectra taken as a function of time. However, $OsCl_6^{-2}$ loss can be followed (see Experimental section). Table II shows the rate constants, obtained from first-order rate plots which were linear over *ca.* 7, 8, 25, 33, and 50% reaction, respectively, curvature beyond these limits being in the direction expected from the back reaction, with increasing amounts of black precipitate observed with decreasing acidity.[21] From 1.32 to 0.01 *F* H^+ the rate of $OsCl_6^{-2}$ loss increases considerably, which in the absence of similar results in HNO_3 medium (Table I) cannot be attributed to base hydrolysis of $OsCl_6^{-2}$. Instead, the effect may arise from formation at these low acid concentrations of a hydrolytically more labile

(18) I. A. Poulsen and C. S. Garner, *J. Am. Chem. Soc.*, **84**, 2032 (1962).
(19) J. C. Chang and C. S. Garner, *Inorg. Chem.*, **4**, 209 (1965).

(20) The black precipitate may be $OsO_2 \cdot 2H_2O$. *E.g.*, O. Ruff and H. Rathsburg, *Ber.*, **50**, 484 (1917), reported the 2-hydrate forms on basifying K_2OsCl_6 solutions and on heating K_2OsCl_6 and $(NH_4)_2OsCl_6$ in water. Attempts by us to analyze the precipitate obtained in $OsCl_6^{-2}$–HCl reaction mixtures gave uncertain results, probably because of strong absorption of NH_4Cl and other salts by the precipitate, a difficulty noted for $OsO_2 \cdot 2H_2O$ by others.

(21) Despite the constancy of (Cl^-), the contribution of the back reaction decreases with decreasing acidity because more $Os(OH_2)Cl_5^-$ is removed to form black precipitate, and hence good first-order rate plots are obtained over an increasing extent of reaction.

lower oxidation state of osmium.[22] *E.g.*, $OsCl_6^{-3}$ might form in small amount by reduction of $OsCl_6^{-2}$ by Cl^-. Some evidence[18,23] exists for catalysis of $IrCl_6^{-2}$ aquation in HCl medium through a slight reduction to $IrCl_6^{-3}$, which is known to aquate much faster at 50° than $IrCl_6^{-2}$ and the aquation product of which is readily oxidized to the observed $Ir(OH)_2Cl_5^-$ product by Cl_2 formed in the system.

TABLE II

ACID DEPENDENCE OF LOSS OF $OsCl_6^{-2}$ IN HCl AT 79.53 ± 0.03°, $(Cl^-) = 1.32$ *F*, $\mu = 1.32$ (NaCl)

(HCl), *F*	$(OsCl_6^{-2})_0$, m*F*	10^6k_C, sec.$^{-1}$
1.32	7.40	4.05
1.32	5.24	4.29
0.12	3.89	4.54
0.030	4.28	15.7
0.012	4.14	60.

To test the idea of catalysis by a more labile lower oxidation state we examined the rate of $OsCl_6^{-2}$ loss in 0.016 *F* HCl–0.48 *F* NaCl at 80° with and without added low concentrations of oxidizing agents which might be expected to oxidize such an intermediate reasonably rapidly. The results are given in Table III. The rate plots were accurately first order as far as reaction was followed, namely, 7–15% reaction (3% and 2% for Fe^{+3} and MnO_4^- runs).

TABLE III

EFFECT OF OXIDIZING AGENTS ON RATE OF LOSS OF $OsCl_6^{-2}$ IN 0.016 *F* HCl–0.48 *F* NaCl AT 79.53 ± 0.03°, $(OsCl_6^{-2})_0$ = 2.6–4.0 m*F*

Oxidant, m*F*	10^6k_O, sec.$^{-1}$	Products[a]
None added	38.4	$Os(OH_2)Cl_5^-$, BP[b] later
$NaNO_3$, 0.14	5.76	OsO_4; BP[b] after 4% rxn.
0.32	4.55	OsO_4
1.8	3.75	OsO_4
490.[c]	3.58	OsO_4
Cl_2, satd.	5.39	OsO_4
$KMnO_4$, 2.3	3.27	OsO_4
$CuCl_2$, 0.12	22.0	BP[b]
1.2	10.0	BP[b]
4.1	5.2	BP[b]
$FeCl_3$, 1.1	3.2	OsO_4

[a] Major products over first 2–15% reaction. [b] Black precipitate (see footnote 20). [c] 0.010 *F* HNO_3–0.49 *F* $NaNO_3$, no Cl^- added.

At low acidities and sufficiently high oxidant concentrations the rate of $OsCl_6^{-2}$ loss is decreased to essentially the same value found in the oxidizing NO_3^- medium at the same ionic strength, and the major product is then usually OsO_4; if the oxidant concentration is lower, the $OsCl_6^{-2}$ disappearance is slowed to a lesser extent and the products include more black precipitate and less OsO_4.

An alternative or concurrent cause of the increased rate of $OsCl_6^{-2}$ loss in Cl^- medium of low acidity may be a heterogeneous catalysis by the black precipitate or colloidal products which precede the precipitation, the amounts of which increase with decreasing acidity.[24] The efficacy of the oxidants of Table III might then arise from oxidation of the secondary products which produce colloids or a precipitate. A partial argument against this hypothesis is the fact that black precipitate (and earlier opalescence) is a major product when the oxidant is 0.14 m*F* $NaNO_3$ or 4.1 m*F* $CuCl_2$, and yet k_O is nearly as small as k_N in comparable NO_3^- medium. Since our interest was in the noncatalyzed aquation of $OsCl_6^{-2}$ we have not further investigated the catalysis.

That the rate-determining step in both Cl^- and NO_3^- media of pH 1 to >5 is the same, namely aquation of $OsCl_6^{-2}$ (forward reaction 1, Introduction), is strongly implied by the following facts: (1) rates of $OsCl_6^{-2}$ loss in NO_3^- medium are constant over the pH range 1 to >5 (Table I) and agree within *ca.* 10% with the rates in Cl^- medium to which sufficient effective oxidant has been added (Table III), (2) this rate is essentially the same as the limiting rate approached with decreasing pH in Cl^- medium in the absence of added oxidant (Table II), and (3) $Os(OH_2)Cl_5^-$ and Cl^- are the only reaction products found in Cl^- medium up to *ca.* 5 hr. at 80°. In NO_3^- medium this rate-determining step is followed quickly by oxidation of the first-formed $Os(OH_2)Cl_5^-$ to OsO_4. Hence, we may take $k_1 = 3.5 \times 10^{-6}$ sec.$^{-1}$ ($t_{1/2}$ = 55 hr.) for aquation of $OsCl_6^{-2}$ in HNO_3 or HCl of pH up to at least 5 at 79.53° in the dark, essentially independent of ionic strength from 0.5 to 1.32.

The rate of aquation of $OsCl_6^{-2}$ was also determined in 0.010 *F* HNO_3–1.31 *F* $NaNO_3$ at two other temperatures, 69.91 ± 0.05° and 89.41 ± 0.05°, giving 0.945 and 12.9 sec.$^{-1}$, respectively, for 10^6k_1. The three k_1 values give an excellent Arrhenius plot, from which were calculated $E_a = 33.1 \pm 0.6$ kcal. mole^{-1} and log $pZ = 15.1 \pm 0.4$ (sec.$^{-1}$).

Rate of Cl^- Anation of $Os(OH_2)Cl_4^-$.—Table IV presents the pseudo-first-order rate constants k'_{-1} for Cl^- anation of $Os(OH_2)Cl_5^-$ (reverse reaction 1, Introduction) at 79.53° and the second-order rate constants $k_{-1} = k'_{-1}/(Cl^-)$ calculated from the average of each pair of k'_{-1} values with (Cl^-) taken equal to the Cl^- formality. The first-order plots were linear over 40–65% reaction (28–41% in 2.49 *F* HCl). Spectral scans over the first 3.1–5.8 hr. gave good isosbestic points at 346–358 mμ (a_M = 7100–5450 M^{-1} cm.$^{-1}$), 385–386 mμ (a_M = 2890–3180 M^{-1} cm.$^{-1}$), and 418–425 mμ (a_M = 1000–760 M^{-1} cm.$^{-1}$), in satisfactory agreement with the values expected for the $Os(OH_2)Cl_5^-$–$OsCl_6^{-2}$ system (Figure 1), namely, 348–355 mμ (a_M = 7100–5900 M^{-1} cm.$^{-1}$), 386 mμ (a_M = 2840 M^{-1} cm.$^{-1}$), and 418 mμ (a_M = 950 M^{-1} cm.$^{-1}$).

The increase in the first values of k_{-1} in Table IV could be related to the increase in either H^+ or Cl^- concentration or ionic strength (in this system (Cl^-) and μ cannot be varied independently). The near agreement of k_{-1} for the first and last runs (which have the same (H^+), but different (Cl^-) and μ) and the large

(22) We are indebted to Professor Henry Taube for this suggestion.

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

(24) This possibility was suggested by one of the referees.

TABLE IV

RATE OF Cl^- ANATION OF $Os(OH_2)Cl_5^-$ AT 79.53 ± 0.03°, $(Os(OH_2)Cl_5^-)_0$ = 0.01–0.02 m*F*, μ = (Cl^-)

(Cl^-), *F*	$10^5k'_{-1}$, sec.$^{-1}$	10^5k_{-1} M^{-1} sec.$^{-1}$
2.49[a]	2.51,[c] 2.68[d]	1.01
3.31[a]	5.36,[c] 5.37[d]	1.62
3.80[a]	7.88,[c] 7.12[d]	1.97
3.79[b]	4.48,[c] 4.22[d]	1.15

[a] HCl, except 0.04 *F* in KCl. [b] 2.46 *F* HCl–1.33 *F* KCl. [c] Change in absorbancy at 370 mμ, A_∞ that of $OsCl_6^{-2}$. [d] $OsCl_6^{-2}$ determined after destruction of all other Os species by NO_3^- at 25°.

difference in k_{-1} between the last two runs (which have the same (Cl^-) and μ, but different (H^+)) suggest the effect is probably largely a H^+ ion effect.[25] The origin of such an effect is not clear, since $Os(OH)_2Cl_5^-$ is unlikely to exhibit acid dissociation at such high acidities. A probably minor complication is the competition of $Os(OH_2)Cl_5^-$ aquation with its anation; details of the spectral scans at 2.5 and 3.3 *F* Cl^- (where aquation competes more than at 3.8 *F* Cl^-) suggest small amounts of a third Os species even though the isosbestic points are compatible with the presence of only $Os(OH_2)Cl_5^-$ and $OsCl_6^{-2}$.

Empirically we can take k_{-1} as *ca.* 2×10^{-5} M^{-1} sec.$^{-1}$ in 3.3–3.8 *F* HCl at 80°. This value is only of very approximate validity in the concentration range for which the $OsCl_6^{-2}$ aquation k_1 was evaluated, and calculation of an equilibrium constant is not warranted.

Discussion

From the rate data of Dreyer and Dreyer[3] on isotopic exchange of $OsCl_6^{*-2}$ with Cl^- in 8.8 *F* HCl at 80° we have calculated an exchange rate constant of 3.1×10^{-6} sec.$^{-1}$. The near agreement with our $k_1 = 3.5 \times 10^{-6}$ sec.$^{-1}$ for $OsCl_6^{-2}$ aquation in 0.00001–0.1 *F* HCl or HNO_3 (μ = 0.5–1.32) at 80° suggests that direct bimolecular exchange contributes negligibly to the above exchange, the appearance of Cl^{*-} in the HCl apparently arising mainly from $OsCl_6^{-2}$ aquation. Their exchange E_a (30 kcal.) is also approximately the same as the E_a (33.1 ± 0.6 kcal.) we find for $OsCl_6^{-2}$ aquation.

Little published work on aquation rates exists for other 5d MX_6 complexes. Aquation of $IrCl_6^{-2}$ was studied by Martinez,[23] but possible catalysis by an $IrCl_6^{-3}$ intermediate implies that the aquation rate constant found at 50° in 0.5–2.8 *F* $HClO_4$ (μ = 1.32–4.91, $NaClO_4$), $(1.01 \pm 0.03) \times 10^{-6}$ sec.$^{-1}$, may be only an upper limit and her E_a of 20.2 ± 0.9 kcal. may be too small. Poulsen and Garner[18] found 2×10^{-4} sec.$^{-1}$ for the $IrCl_6^{-3}$ aquation rate constant at 50° in 2.5 *F* $HClO_4$ (μ = 3.7, $NaClO_4$), with $E_a = 30.4 \pm 2.0$ kcal. and log $pZ = 17.5 \pm 1.8$ (sec.$^{-1}$). Thus, at 50° $OsCl_6^{-2}$ ($k_1 = (4.8 \pm 0.3) \times 10^{-8}$ sec.$^{-1}$ by calculation from 70° k_1 and E_a) aquates $\leqslant$21-fold slower than $IrCl_6^{-2}$ and 4000-fold slower than $IrCl_6^{-3}$.

Present theories are inadequate to rationalize such behavior fully, and much more experimental work is needed on 5d complexes of this type. Crystal-field theory predicts that activation energies for substitution reactions of strong-field ("inner-orbital") octahedral d complexes increase in the order $d^5 > d^4 > d^3 > d^6$ by either an SN1 or SN2 mechanism.[26] Factors other than those arising from differences in crystal-field stabilization energy are not considered, and exceptions to this rule are known. If we compare the above Ir(IV) d^5 and Os(IV) d^4 complexes, where the formal charge is the same on the central metal atom, we see the d^5 complex does apparently have the smaller activation energy. The d^6 $IrCl_6^{-3}$ complex, however, has a lower activation energy than the d^4 $OsCl_6^{-2}$; the former has a lower formal charge on the central metal atom which could facilitate loss of Cl^- in the transition state, although such an effect is often considered less important than crystal-field effects. Clearly more data on substitution rates of 5d complexes are needed.

We had originally hoped the current study of $OsCl_6^{-2}$ was to be the first in an investigation of successive aquation steps of the chloroaquo species. The early appearance of colloids and precipitation in HCl medium makes further study unattractive.

(25) In ref. 18 it is shown that the second-order rate constant for Cl^- anation of $Ir(OH_2)Cl_5^{-2}$ at 50° is doubled on going from 1.0 to 2.5 *F* H^+ at 1 *F* Cl^- and μ = 3.4–3.7 (an effect of the same direction and approximate magnitude as we find for the Os(IV) analog), but is nearly constant when μ increases from 2.2 to 3.4 at 1 *F* H^+ and 1–3.4 *F* Cl^-.

(26) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 110. The calculations apparently have been made for the 3d transition elements.