

Electrochemistry of *trans*-Dioxotetrachloroosmate(VI). Reduction Mechanism, a New Route to Aquachloroosmate(III) and -(IV) Species

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The electrochemistry of osmium in the oxidation states III, IV, and VI in hydrochloric acid media is examined by using a variety of electrochemical techniques and a rank-matrix treatment of the spectrophotometric data. The electrochemical reduction of oxoosmate(VI) species forms is irreversible and is preceded by a rate-limiting chemical reaction and followed by a post associated chemical redox reaction to give Os(IV) species. The electron-transfer proceeds by a single three-electron step concerted with proton transfers through the $[\text{Os}^{\text{VI}}\text{O}_2\text{Cl}_4]^{2-}$ species to give transient $[\text{Os}^{\text{III}}\text{Cl}_4(\text{H}_2\text{O})_2]^-$. At high $[\text{Cl}^-]$ values the Os(III) species reacts with Os(VI) species to give monomeric $[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2]$, which is more easily reducible than the starting material. At low $[\text{HCl}]$ values, another redox reaction competes with the latter reaction and gives the dimeric $\mu\text{-oxo } [[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2]_2\text{O}]^{2-}$, which is more difficult to reduce than the starting material. The inertness of the chloro complexes at the Os(IV) state permits generation in solution of $[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2]$, $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2]_2\text{O}]^{2-}$, $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$, and $[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$ by electrochemical means. The more labile Os(III) complexes, $[\text{Os}^{\text{III}}\text{Cl}_n(\text{H}_2\text{O})_{6-n}]^{3-n}$ ($n = 4-6$), are generated as a mixture which depends on chloride concentration exclusively.

The chloro complexes of the platinum metals are of considerable importance in the preparative and analytical chemistry of these elements.¹ Moreover, they are used as starting materials in the preparation of many new types of compounds used as catalysts or catalytic precursors of industrial reactions.²⁻⁵ While the chloro complex chemistry of iridium, rhodium, ruthenium,¹² etc. has been widely investigated, the development of the aqueous chemistry of osmium has been limited by a scarcity of tractable starting materials.¹³⁻¹⁵ Electrochemistry may therefore be considered as a valuable source of data for the aqueous chemistry of osmium. The electrochemical behavior of osmium has received attention for more than 30 years.¹⁶⁻²⁰ Most of the studies were polarographic studies of osmium tetroxide at a dropping-mercury electrode in various media. In some instances the available data are inadequate and contradictory. It is only in recent years that some information has been obtained on the behavior of oxoosmate(VI) at a platinum-rotating-disk electrode.²¹ Among the oxoosmate(VI), the chloroosmate(VI) have been prepared by Wintrebert²² and studied by several authors.²³⁻²⁶ A recent work²⁷ demonstrates in solution the existence of two chlorooxoosmate(VI) species in the $[\text{Cl}^-]$ range 1.0-8.25 M. Below 1.0 M Cl^- , supplementary species appear,²⁸ and beyond 8.25 M HCl , spontaneous reduction of $[\text{OsO}_2\text{Cl}_4]^{2-}$ occurs by chloride ion at room temperature.²⁷ The present work attempts to provide a detailed analysis of the reduction mechanism of chlorooxoosmates(VI). In this connection the effect of respective chloride and proton concentrations has been systematically investigated. Controlled-potential electrolysis and coulometry have also been used to prepare and characterize in solution the reduced states of chlorooxoosmate(VI). Until now, for the Os(IV) state two products have been separated from the hydrolysis mixture of $[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$ by anion exchange or ionophoresis. The hydrolysis products are reported^{29,30} to be $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ and $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2]_2\text{O}]^{2-}$; this latter complex was the apparent end product. Nevertheless recently³¹ new chloroaquohydroxoosmate(IV) species have been reported in the hydrolysis of $[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$ and in chemical reduction of osmium tetroxide by iron(II) sulfate. The Os(III) state has been less investigated; only $[\text{Os}^{\text{III}}\text{Cl}_6]^{3-}$ and $[\text{Os}^{\text{III}}\text{Cl}_5(\text{H}_2\text{O})]^{2-}$ have been previously cited.³²⁻³⁴

Experimental Section

Instrumentation. UV and visible absorption spectra were recorded with a Jobin Yvon DUOSPAC 203 spectrophotometer or a Jouan

R 185 spectrophotometer. Cyclic voltammetric data (CV) were obtained with a Tacussel PRT 20-10 potentiostat in combination with

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a Tacussel UAP4 universal programmer. Slow-scan (0.05–0.20 V s⁻¹) CV were reported on a Sefram TGM 164 X-Y recorder. Fast-scan CV were obtained from photographs of the trace from a Tektronix R 5111 storage oscilloscope.

Rotating-disk-electrode voltammetric data (RDEV) were performed with a Tacussel PRG 2 instrument. Controlled-potential electrolysis (CPE) were carried out with a Tacussel PRT 100-1 potentiostat in combination with a Tacussel ING 5 coulometer; the potential was controlled with a Tacussel ISIS 4000 instrument.

Cell and Electrodes. All experiments were carried out in a thermostated flask in an argon atmosphere at 25 ± 0.1 °C. A conventional three-electrode three-compartment cell was used; additionally the working electrode chamber held a large-area electrode to allow coulometric experiments as desired. The RDEV was achieved with a platinum or vitreous carbon electrode. A platinum wire was used as an auxiliary electrode, and all potentials were referred to the saturated calomel electrode (SCE), whose potential is +0.24 V vs. the normal hydrogen electrode.

Chemicals. Potassium osmate(VI), K₂[Os^{VI}O₂(OH)₄] was prepared by ethanol reduction of OsO₄ in 1 M KOH. The Os(VI) solutions in chloride media are obtained by additions of aliquots of K₂[Os^{VI}O₂(OH)₄] to an aqueous medium containing HCl and LiCl with various proportions. All the solutions were prepared from twice distilled water.

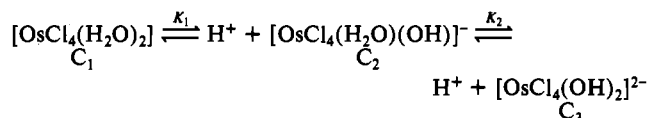
The electrochemical experiments on osmate(III) and -(IV) species were performed on solutions obtained by introducing the requisite volumes of stock solutions in the desired medium. The stock solutions were prepared by electroreduction of Os(VI).

pK_a Determination. The pK_a values for the deprotonation equilibria of Os(IV) species were determined spectrophotometrically at 10 ± 0.2 °C in water with 4.0 M NaClO₄.

An aqueous solution containing the supporting electrolyte with the requisite [H⁺] value was equilibrated at 10 °C. (The Hammett acidity function H₀³⁶ is used instead of pH at high [H⁺] value.) The stock solution of Os(IV), obtained as described below in this work, was equilibrated in the same bath. The reaction was initiated by rapidly mixing the requisite volume of the Os(IV) stock solution with 50 mL of the supporting solution. The spectrophotometric measurements were performed as soon as possible to prevent secondary reactions (vide infra). The data for pK_a calculations were selected in the H₀ range where the deprotonations were reversible.

The simultaneous determination of the pK_a value and the molar extinction coefficient ε_i of absorbing species C_i were obtained from the spectrophotometric data by using a least-squares refinement program that minimizes the Σ₁^N(ε_{obsd} - ε_{calcd}) function (N = number of data points) (see supplementary material).

$$\bar{\epsilon}_{\text{calcd}} = \frac{\epsilon_1[\text{H}^+]^2 + \epsilon_2K_1[\text{H}^+] + \epsilon_3K_1K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}$$



The average molar extinction coefficient is defined as $\bar{\epsilon}_{\text{obsd}} = A/C_0L$ in which *A* is the absorbance, C₀ the analytical concentration of osmium(IV), and *L* the spectrophotometer cell length in centimeters. The procedure computed also the standard deviation. The final repartition of the residuals $\bar{\epsilon}_{\text{obsd}} - \bar{\epsilon}_{\text{calcd}}$ indicated the absence of systematic errors; with the best values of K₁, K₂, and ε_i, we find Σ₁^N(ε_{obsd} - ε_{calcd})/ε_{calcd} · N < 5%.

Rank-Matrix Analysis of Spectrophotometric Data. During the CPE, UV-vis spectra were recorded after various stages of reduction. It became desirable to know the number of species present in the solution in order to fit the spectrophotometric data to a detailed analysis. Consequently we felt that a method of matrix analysis could be used.³⁷ For the application of this method one measures a set

Table I. Cyclic Voltammetric Data for [Os^{VI}O₂Cl₄]²⁻ in HCl-LiCl Aqueous Solution (9 × 10⁻⁴ M) at 0.05 V s⁻¹ on a Pt Electrode

[Cl ⁻], M	[H ⁺], M	E _{pc} ^a	i _{pc} ^a , μA	E _{pc} ^b	E _{pa} ^b	i _{pc} ^b / i _{pa}
6.17	6.17	0.00	60	0.14	0.22	1
5.8	5.8	0.00	55	0.14	0.22	1
4.5	4.5 ^c	-0.01	48	0.14	0.22	1
3.35	3.35	ill defined		0.14	0.24	1
2.2	2.2	ill defined		0.15	0.26	1
1.1	1.1	ill defined		0.15	0.27	1
1.1	1.1 ^c	ill defined		0.16	0.26	1
5.0	0.4	-0.08 ^d	30	0.15	0.26	1
7.4	0.4	-0.08 ^d	30	0.15	0.26	1
7.4	1.0	-0.05	40	0.14	0.25	1
7.4	3.4	-0.03	51	0.13	0.24	1
7.4	6.0	0.00	72	0.14	0.22	1

^a First scan in V vs. SCE. ^b After consecutive sweeps.

^c Vitreous carbon electrode. ^d Shoulder.

of absorbance at different wavelengths *i* at several stages of reduction *j*. They are then arranged in a rectangular matrix A_{*ij*}, and the number of independent variables is determined from the rank (*r*) of the matrix, with a statistical criterion of the experimental errors (σ). If the concentrations of one or more species can be expressed as a linear combination of those of other species in all experiments, the rank *r* of the matrix will be less than the species number. This feature can be suppressed by choosing different concentration levels in some experiments.

Results

The electrochemical reduction of Os(VI) in chloride media at platinum and vitreous-carbon electrodes was studied by means of rotating-disk-electrode voltammetry, cyclic voltammetry, and coulometry. Potential values are given with respect to the saturated aqueous calomel electrode SCE.

1. RDE Voltammetry. The RDEV experiments were performed on solutions of Os(VI) in various chloride media. No oxidation wave is obtained, and the single reduction wave is poorly developed, extending over several hundred millivolts. The ill-defined limiting current between +0.1 and -0.2 V corresponds to about 40% at most of that expected for a diffusion-controlled one-electron reduction reaction. The variations of the ill-defined limiting current with [Cl⁻] and [H⁺] are not striking, even taking into account viscosities of the supporting electrolytes. This phenomenon may be in accordance with a reaction sequence involving chemical reactions preceding the electron transfer.

2. Cyclic Voltammetry. The CV experiments were carried out on a platinum or vitreous carbon electrodes at several [H⁺] and [Cl⁻] ranging respectively from 0.4 to 7.4 M. [H⁺] and [Cl⁻] abbreviations are used for the respective concentration values of proton and chloride; the respective counterions are ClO₄⁻ and Li⁺. When [H⁺] and [Cl⁻] vary simultaneously, the symbol [HCl] is used. The voltammograms obtained on platinum and on vitreous-carbon electrodes at the same [H⁺] and [Cl⁻] values exhibit little difference. This leads to the conclusion that the charge transfer reflects the intrinsic properties of the reduction of Os(VI) with negligible influence of the electrode material on the nature of the reduced species.

The important features of the *i*-*E* patterns (Figure 1) after the first cathodic scan are as follows: (i) a single reduction peak which is considerably drawn out and rounded particularly at low [H⁺] and [Cl⁻] values and at high scan rates (in this case, the reduction occurs only as a shoulder on the background current rise); (ii) the peak intensities increase with [H⁺] and [Cl⁻] increases; (iii) a peak potential shift in the cathodic direction with increased sweep rate. The general aspect of the CV curves and their variations with [H⁺], [Cl⁻], and the sweep rate (Table I) is typical of a reduction process involving an homogeneous chemical reaction that precedes the irreversible

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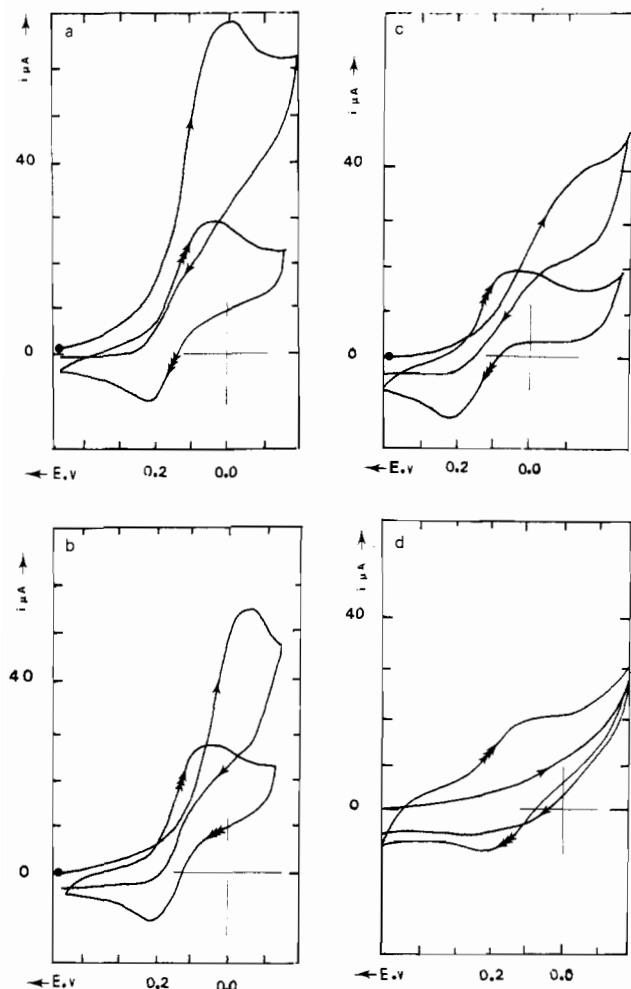
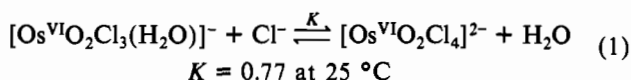


Figure 1. Cyclic voltammetry of the Os(VI) system on a platinum electrode in chloride media: (a) 6 M H⁺ and 7.4 M Cl⁻; (b) 3.4 M H⁺ and 7.4 M Cl⁻; (c) 0.4 M H⁺ and 7.4 M Cl⁻; (d) 1.09 M H⁺ and 1.09 M Cl⁻. Sweep rate = 0.05 V s⁻¹. [Os(VI)] = 9 × 10⁻⁴ M. The single arrow represents after the first scan and the triple arrow after multiple scans.

electron-transfer step. A previous work²⁷ has determined by spectrophotometry the equilibrium constant corresponding to reaction 1.



This equilibrium occurs in the [Cl⁻] experimental range of the present work. At the same [H⁺] value the magnitude of the reduction peak increases with a [Cl⁻] increase and concomitantly with a [Os^{VI}O₂Cl₄]²⁻ increase (Table I). This suggests that in the experimental [Cl⁻] range the reduction occurs through the [Os^{VI}O₂Cl₄]²⁻ species exclusively although the less reducible [Os^{VI}O₂Cl₃(H₂O)]⁻ species predominates still at equilibrium in 1 M HCl, for example. This latter form reduces probably in the background current, but the reduction can occur at less cathodic potential through its prior conversion into the [Os^{VI}O₂Cl₄]²⁻ form. The peak potential corresponding to the [Os^{VI}O₂Cl₄]²⁻ reduction occurs at less cathodic potential with high [H⁺] values. The shift of E_{pc} due to the change in [H⁺] is in good agreement with the general electrode reaction $\text{Ox} + ne^- + m\text{H}^+ \rightarrow \text{Red}$.^{38,39} The height of the peak increases also with [H⁺] increase. It is not possible to propose

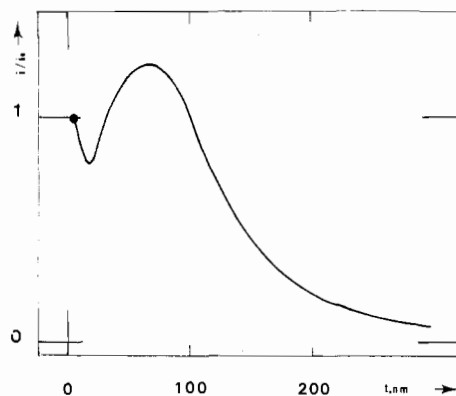


Figure 2. i/i_0 vs. t during the controlled-potential electrolysis at $E = -0.1$ V vs. SCE in 3.3 M HCl; [Os] = 10⁻² M.

an extensive interpretation. However, the [H⁺] dependence can be attributed to the proton-coupled electron-transfer reactions and also perhaps to the proton catalysis of the chloride anation of reaction 1 to give the more easily reducible species. Theoretically the height of the peak reflects the kinetics and thermodynamics of the chemical reactions.⁴⁰⁻⁴³ Unfortunately, it is not possible to obtain the kinetic parameters from the CV data. Indeed a fast post associated chemical reaction (vide infra) occurs on the time scale of the CV, after the electron transfer, and greatly complicates the analysis of the CV curves.

On the reverse (anodic-going) sweep a single peak appears (Figure 1 and Table I). The current, $i_{pA}/v^{1/2}$, of the anodic peak decreases when the sweep rate v decreases. At slow scan rates ($v < 0.1$ V s⁻¹), no anodic peak is detected $i_{pA}/v^{1/2} \rightarrow 0$.

On the second (cathodic-going) sweep a new cathodic peak develops at 0.14 V with the concomitant disappearance of the peak at 0.00 V (6.17 M HCl), which suggests that a new electroactive species is formed following the first reduction peak. After a few consecutive sweeps, the magnitude of the new cathodic and anodic peaks increases to yield about a 1:1 peak current ratio (Figure 1). The separation (ΔE_p) between cathodic and anodic peaks lies in the range 120–80 mV (Table I). This clearly establishes the presence at the electrode of an almost reversible electron-transfer process at least in very acidic media. It is tempting to assign these peaks to the Os(IV)/Os(III) couple.

3. Controlled-Potential Electrolysis (CPE). The following coulometric experiments were performed to establish two important aspects of the reduction mechanism: the total number of electrons consumed by the *trans*-dioxotetrachloroosmate(2-) in the overall reduction process and the identity of the electrochemical reduction products. In addition current-time behavior during exhaustive electrolysis was used as corroborative evidence for the reduction mechanism. Figure 2 shows a plot of i/I_0 vs. t for the constant-potential reduction at -0.1 V at a platinum-grid electrode of Os(VI) solution in chloride media. The controlled-potential electrolysis proceeded abnormally but after several hours 3 faradays/mol of Os(VI) were consumed at high [Cl⁻] values. In Figure 2 there are clearly at least two portions in the current-time curve obtained in concentrated chloride media. The electrolysis current exhibits an unusual behavior: after a short time the current increases. The current-time data obtained after the maximum are in good accordance with the logarithmic law $\log(i/I_0)$ vs. t plot, which gives a straight line. It should be noted that the

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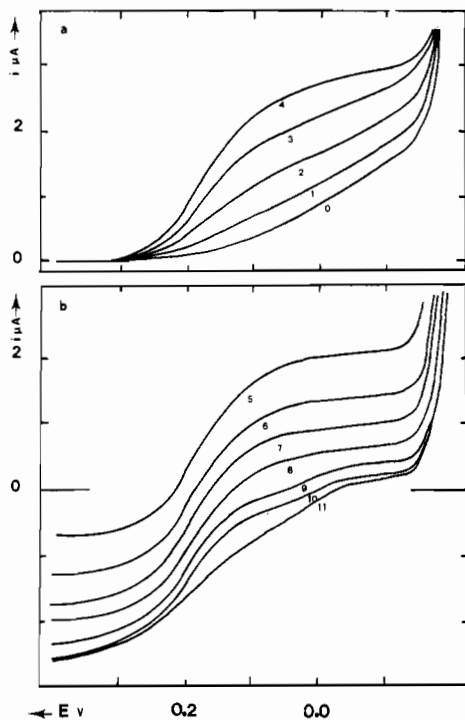


Figure 3. Rotating-disk-electrode voltammograms resulting from the exhaustive electrolysis at $E = -0.1$ V vs. SCE of Os(VI) in 4.45 M HCl; $[\text{Os}] = 10^{-3}$ M. The curves numbered 0–11 correspond respectively to 0, 0.4, 0.9, 1.4, 1.9, 2.1, 2.4, 2.5, 2.7, 2.8, 2.9, and 3.0 faradays/mol.

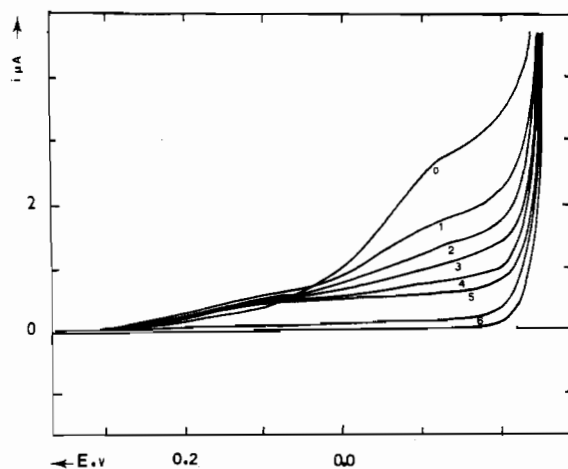


Figure 4. Rotating-disk-electrode voltammograms resulting from the exhaustive electrolysis at $E = -0.1$ V vs. SCE of Os(VI) in 1.09 M HCl; $[\text{Os}] = 10^{-3}$ M. The curves numbered 0–6 correspond respectively to 0, 0.2, 0.6, 1.1, 1.6, 1.8, and 2.05 faradays/mol.

shape of the curve $I(t)$ depends on the $[\text{H}^+]$ and $[\text{Cl}^-]$ respective values, and the current maximum at $E = -0.1$ V corresponds to less than 2 faradays/mol and at most to 2 faradays/mol.

At lower $[\text{HCl}]$ values the controlled-potential electrolysis proceeded more and more slowly and the unusual current maximum disappears progressively and the reduction consumed less than 3 faradays. In 1 M HCl 2 faradays/mol of Os(VI) were consumed. To obtain more information about this abnormal behavior it was therefore desirable to undertake RDEV, CV, and spectrophotometric experiments during the course of the reduction of Os(VI).

Two different RDEV behaviors are observed according to the $[\text{Cl}^-]$ value. Two typical examples selected in a series of experiments at $[\text{Cl}^-]$ ranging from 1.09 to 8.25 M are given on Figures 3 and 4, which show the curves obtained at 4.45

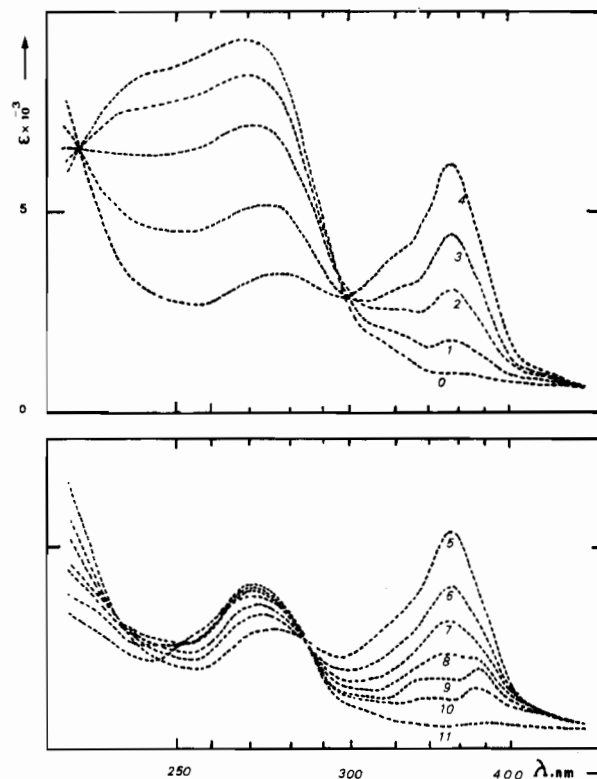


Figure 5. Spectral changes resulting from the exhaustive electrolysis at $E = -0.1$ V vs. SCE of Os(VI) in 4.45 M HCl; $[\text{Os}] = 10^{-3}$ M. The spectra numbered 0–11 correspond respectively to 0, 0.4, 0.9, 1.4, 1.9, 2.1, 2.4, 2.5, 2.7, 2.8, 2.9, and 3.0 faradays/mol.

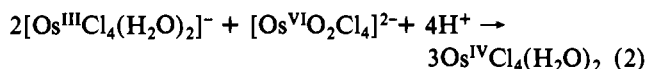
and 1.09 M HCl for various stages of reduction of Os(VI). At a high $[\text{Cl}^-]$ value after an electrolysis time corresponding to less than 2 faradays/mol, no anodic wave portion is observed. The ill-defined limiting current of Os(VI) evolves to a well-defined wave with concomitant anodic shift of $E_{1/2}$ from -0.10 to $+0.19$ V in 4.45 M HCl. The limiting current corresponds to the expected diffusion-controlled one-electron reduction reaction. This new electroactive species is attributed to an Os(IV) species (vide infra). It should be noted that the maximum of the amperometric intensity of $+0.1$ V corresponds strictly to 2 faradays/mol in concentrated chloride media. However, the maximum of the amperometric intensity at -0.1 V corresponds generally to less than 2 faradays/mol. After an electrolysis time corresponding to more than 2 faradays/mol, the expected RDEV behavior of a reversible one-electron transfer is observed. The $E_{1/2}$ and the overall height of the wave are approximately constant. Nevertheless during the second part of the electrolysis small changes occur progressively on the anodic portion of the voltammograms particularly at high $[\text{Cl}^-]$ values and new minor waves appear at more reducing potential (Figure 3).

The transient species obtained during the exhaustive electrolysis is attributed to the monomeric Os(IV) species $\text{Os}^{\text{IV}}\text{-Cl}_4(\text{H}_2\text{O})_2$. The reoxidation of the resulting solution at $+0.40$ V consumes 1 faraday/mol (0.97), and $E_{1/2}$ of the major wave remains constant.

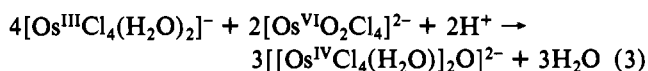
At lower $[\text{Cl}^-]$ values the rate of the electrolysis at -0.1 V decreases. The height of the Os(IV)/Os(III) wave $E_{1/2} = 0.19$ V becomes less and less important with a $[\text{Cl}^-]$ decrease; this wave disappears at low $[\text{Cl}^-]$ values as shown in Figure 5. In 1.09 M HCl the exhaustive electrolysis proceeds smoothly at -0.1 V with the consumption of 2 faradays/mol of Os(VI) (2.07) to yield a solution of Os(IV). Indeed the UV-visible absorption spectrum of the reduced solution is identical with that reported for $[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2]^{2-}$ by Miano and Garner.²⁹ This species, which is supposed to be dimeric, is not

reducible at the platinum electrode at -0.1 V.

The essential features displayed by the RDE voltammograms represented in Figures 3 and 4 and those obtained in the same $[\text{Cl}^-]$ range are the following: (i) At high $[\text{Cl}^-]$ values the monomeric Os(IV) intermediate is produced by the chemical oxidation of the monomeric Os(III) species generated at the electrode by the Os(VI) species (eq 2).



The comproportionation reaction 2 seems rapid and quantitative under the conditions of the controlled-potential electrolysis; $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ is more easily reducible than the starting material. In the $[\text{H}^+]$ interval 0.4 – 8.25 M, Os(IV) is stable with respect to disproportionation. (ii) At low $[\text{HCl}]$ values the oxo-bridge binuclear $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})]_2\text{O}]^{2-}$ seems produced by a redox-coupled olation reaction. As it is shown below, the conversion of the monomeric form of Os(IV) to the dimeric one does not occur rapidly in these media by an olation reaction. Reaction 3 is relatively rapid on the time scale of



the CPE but not on the time scale of the CV (Figure 1). Moreover, reaction 3 seems quantitative in 1 M HCl but competes with reaction 2 at higher HCl values. The oxo-bridged dimer $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})]_2\text{O}]^{2-}$ is less easily reducible than the starting material.

The cyclic voltammograms run during the electroreduction of Os(VI) were studied at a platinum electrode in the same experimental conditions.

The CV results obtained after various stages of reduction corroborate with the RDEV data: (i) At high $[\text{Cl}^-]$ values a new reversible one-electron system appears with $E_{\text{pc}} = 0.14$ V and $E_{\text{pa}} = 0.22$ V for $[\text{HCl}]$ greater than 4.45 M; the peak to peak potential separation is close to the theoretical value of 60 mV which is representative of a Nernstian diffusion-controlled system.^{29,30} (ii) Below 3 M HCl the magnitudes of the anodic and cathodic peaks become smaller, and both peaks have disappeared below 1 M HCl. (iii) The CV curves performed on the reduced solutions are very analogous to the i - E patterns obtained after several consecutive sweeps with Os(VI) as starting material in the corresponding supporting electrolyte and the same scan rate.

The electrochemical data have pointed out evidence for several Os(IV) and Os(III) species in chloride media. It is therefore desirable to determine the number of species and the $[\text{Cl}^-]$ or $[\text{H}^+]$ ranges where a single species makes a major contribution to solution composition. We employed for this purpose a treatment of the spectrophotometric data by a method of rank-matrix analysis.³⁷ The UV-visible spectra were performed after various stages of reduction with conditions identical with those of the electrochemical experiments. As reduction proceeds, spectral changes occur which are typical of the reduction of Os(VI) to Os(IV) and finally to Os(III): the MLCT absorption bands in the vicinity of 350 nm are characteristic of the Os(IV) state^{44,45} and are the best indication of detecting Os(IV).

Two typical examples selected in a series of spectrophotometric experiments at $[\text{Cl}^-]$ ranging from 1.09 to 11.7 M are given in Figures 5 and 6.

Matrices of absorbance at different wavelengths, at several stages of reduction performed in various chloride media, are

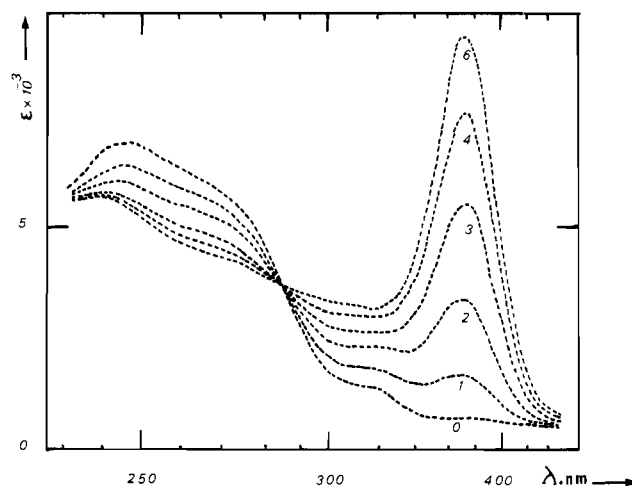


Figure 6. Spectral changes resulting from the exhaustive electrolysis at $E = -0.1$ V vs. SCE of Os(VI) in 1.09 M HCl; $[\text{Os}] = 10^{-3}$ M. The spectra numbered 0–6 correspond respectively to 0, 0.2, 0.6, 1.1, 1.6, and 2.05 faradays/mol.

Table II. Number of Chloroosmate(IV) Species Produced during the Electrochemical Reduction of Chlorodioxoosmates(VI)

$[\text{Cl}^-]$, M	$[\text{H}^+]$, M	r_1^a (σ)	P^a	r_2^b (σ)	P^b
8.25	8.25	3 (0.01)	2	3 (0.01)	3
6.17	6.17	2 (0.005)	1	2 (0.01)	2
4.45	4.45	2 (0.01)	1	2 (0.01)	2
3.30	3.30	3 (0.01)	2	2 (0.01)	2
2.22	2.22	3 (0.01)	2	2 (0.01)	2
1.09	1.09	2 (0.005)	1	1 (0.01)	1
7.4	0.4	3 (0.01)	2	3 (0.01)	3
7.4	3.0	2 (0.01)	1	2 (0.01)	2
1.09–8.25	0.4–8.25	6 (0.01)	4	4 (0.01)	4
		4 (0.02)	2	3 (0.02)	3

^a r is the rank of the matrix A_{ij} : A , absorbance; i , wavelength; j , solution. r_1 is the first stage of reduction with λ_i 240–440 nm. P is the number of absorbing Os(IV) species and σ the statistical criterion. ^b r_2 is the second stage of reduction with λ_i 350–440 nm.

constructed. The treatment of these rectangular matrices by rank analysis³⁷ (see Experimental Section) gives the data listed in Table II.

As it is pointed out by the electrochemical experiments, two different behaviors are observed according to the appearance or not of Os(III) species. The number P of absorbing Os(IV) species at the first step of the CPE at -0.1 V are listed in Table II.

It is noticeable that the two Os(VI) species are numbered as one species when the measurements are achieved at the same $[\text{Cl}^-]$ values and as two species when the measurements are performed at various $[\text{Cl}^-]$ values. If the wavelengths are limited to 350 – 440 nm, the absorbing Os(IV) species are only taken into account. Indeed the absorbances of Os(VI) and Os(III) species are negligible in this range. During the second step of the CPE of Os(VI), supplementary Os(IV) species appear (Table II). These results are consistent with the electrochemical experiments. The overall number of the major Os(IV) species, involved in the experimental media, is 3 in the first step of the reduction (from Os(VI) to Os(IV)) and 4 in the second step (from Os(IV) to Os(III)). The spectrophotometric results point out the media where a single species makes major contribution to solution composition with a sufficient kinetic stability.

The exhaustive CPE at -0.1 V of Os(VI) in 1.09 M HCl generates a single species with a UV-visible spectrum identical with those reported previously for the dimer $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})]_2\text{O}]^{2-}$. The electrochemical stoichiometry is $n = 2$ by coulometry. At the platinum electrode no reduction wave is

(44) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, Oxford, England, 1962.

(45) C. K. Jorgensen, *Mol. Phys.*, **2**, 309 (1959).

observed; moreover, in the same medium the dimeric species exhibits a single reduction wave at a dropping-mercury electrode ($E_{1/2} = -0.42\text{V}$) (vide infra). The solution is stable over several days at room temperature. The purity of the chloride solution of the dimer (at least 90%) is estimated by spectrophotometric data and RDEV behavior.

The CPE at -0.1 V of Os(VI) in 6.17 M HCl generates a single species when the reduction is stopped at the Os(IV) state (Table II and Figure 6). The electrochemical stoichiometry is $n = 2$ by coulometry. This novel species is attributed to $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ (vide infra).

The purity of the resulting solution (at least 90%) is estimated by spectrophotometric data and by the CV and RDEV behaviors of a seemingly reversible one-electron transfer. The solution is stable over several hours at 5°C .

The CPE at -0.1 V of Os(VI) in 0.4 M H^+ and 7.4 M Cl^- ($n = 2$) generates at room temperature a mixture of two species which evolves to a single species attributed to $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$. Indeed the UV-visible spectrum of the resulting solution is identical with the spectra reported for this species.^{29,30} The purity of the resulting solution (at least 90%) is estimated by spectrophotometric data and by the CV and RDEV behaviors of a reversible one-electron transfer. The solution is stable over several days at room temperature.

It is striking that this latter species can be also generated rapidly in 11.7 M HCl solution by spontaneous chloride chemical reduction of $[\text{Os}^{\text{VI}}\text{O}_2\text{Cl}_4]^{2-}$.²⁷ After electrolysis at $+0.3\text{ V}$ (the oxidized species of chloride are reduced off), the spectral and electrochemical properties of the solutions are characteristic of the single species $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$. The inertness to the substitution reaction of osmate(IV) species allows the obtention of aquochloroosmate(IV) species^{46,47} even at high $[\text{Cl}^-]$ values with notable kinetic stabilities. These kinetic stabilities permit the investigation of the acid-base and redox properties of the Os(IV)-Os(III) system by using spectral and electrochemical techniques.

4. Acid-Base Behavior of Aquoosmates(IV). A fast spectrophotometric titration (Figure 7) shows that $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ is a strong diacid having $\text{p}K_1 = 0.3 \pm 0.2$ and $\text{p}K_2 = 0.8 \pm 0.2$ at 10°C (see Experimental Section) in 4 M NaClO_4 . The $\text{p}K_a$ values are derived by a least-square evaluation of the spectrophotometric data; the fitting procedure also gives the calculated spectra of the three species: $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$, $[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})(\text{OH})]^-$, and $[\text{Os}^{\text{IV}}\text{Cl}_4(\text{OH})_2]^{2-}$. During deprotonation, spectral changes occur $\lambda_{\text{max}} 360\text{ nm}$ ($\epsilon = 7300$) \rightarrow $\lambda_{\text{max}} 324\text{ nm}$ ($\epsilon = 7600$) \rightarrow $\lambda_{\text{max}} 290\text{ nm}$ ($\epsilon \sim 3000$).

The deprotonation of the bound water of $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ occurs in a less acidic range than for the new species $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$. The $\text{p}K_a$ value of $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ is analogous to those reported previously by Preetz and Schätzel³¹ with a product obtained by electrophoresis from an hydrolysis mixture of $[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$ with $\text{p}K_a = 2.3$.³¹

Apparently the remarkably enhanced acidity from $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ to $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ comes from the stabilization of the Os(IV) site electron deficient by $\text{p}(\text{OH}) \rightarrow \text{d}\pi(\text{Os}(\text{IV}))$ electron donation.

The deprotonations of the coordinated water of the dimer $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})]_2\text{O}]^{2-}$ have been reported previously³⁰ and occur in the pH range 2-3. If the deprotonations of the complexes $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ and $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})]_2\text{O}]^{2-}$ do not occur in the $[\text{H}^+]$ range of the electrochemical studies (vide infra) on the other hand, $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ is partially deprotonated at $H_0 = 0$ ($H_0 =$ Hammett function).

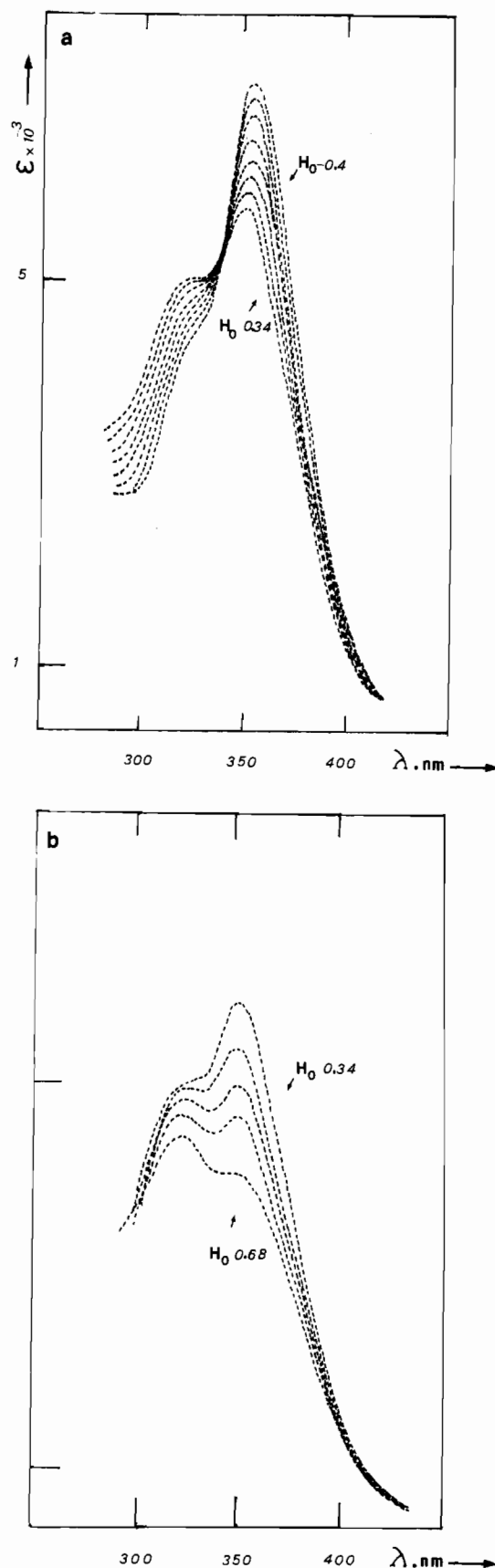


Figure 7. Spectral changes accompanying changes of the acidity H_0 (Hammett acidity function) of $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ in 4.0 M NaClO_4 ; $[\text{Os}] = 10^{-4}\text{ M}$.

Olation Reaction. At room temperature, a solution of $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ introduced in 1 M HClO_4 gives slowly an absorption near 370 nm over several days. The limiting cathodic current of the RDEV wave ($E_{1/2} = +0.19\text{ V}$) of this

(46) W. Preetz and H. J. Walter, *Z. Anorg. Allg. Chem.*, **402**, 169 (1973).

(47) R. Dreyer and I. Dreyer, *Z. Chem.*, **4**, 106 (1964).

(48) G. M. Brown, R. W. Callahan and T. J. Meyer, *Inorg. Chem.*, **14**, 1915 (1975).

(49) B. A. Moyer and T. J. Meyer, *J. Am. Chem. Soc.*, **100**, 360 (1978).

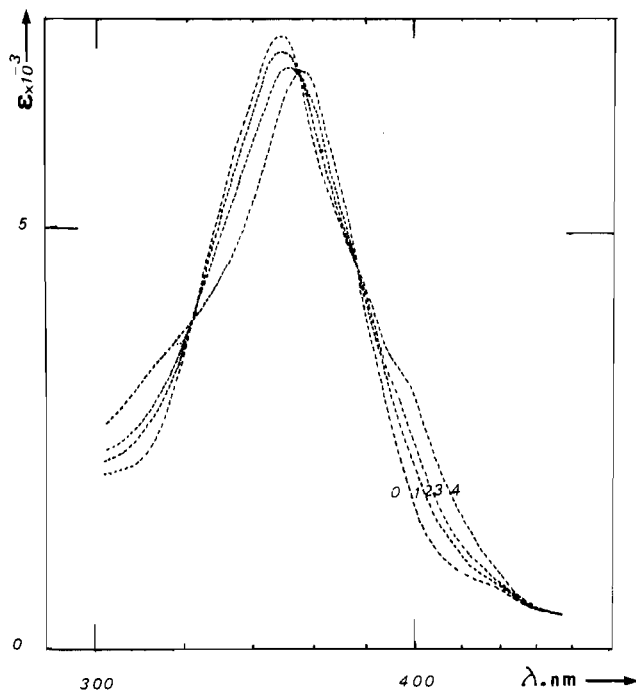
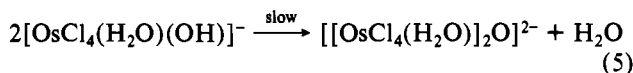
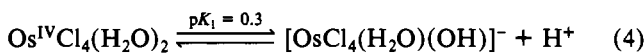


Figure 8. Spectral changes during the course of the anation reaction $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2 + \text{Cl}^- \rightarrow [\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ in 6.17 M HCl at room temperature: 0, time the electrolysis is stopped at 2.0 faradays/mol; 4, after 24 h. The Os(IV) is generated by electrolysis of Os(VI). $[\text{Os}] = 10^{-3}$ M.

solution decreases as the reaction proceeds. These features are in good agreement with a slow olation reaction to give the μ -oxo-bridged binuclear $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})]_2\text{O}]^{2-}$



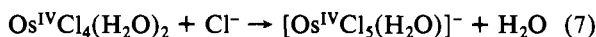
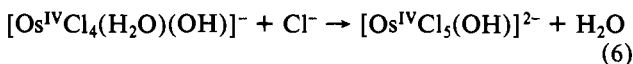
This latter reaction is not reversible. Indeed an addition of HClO_4 in excess does not generate the reverse reaction.

Chloride Anation of $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$. Acid-Base Catalytic Pathway. At room temperature the solution of $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ in 6 M HCl ($\lambda_{\text{max}} 360$ nm, $E_{1/2} = +0.19$ V) upon aging gives finally $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ ($\lambda_{\text{max}} 350$ nm, $E_{1/2} = +0.10$ V).

The reaction is quantitative in 24 h at room temperature (Figure 8). However, in 0.4 M H^+ and 7.4 M Cl^- , the reaction is quantitative in 2 h.

Although kinetic data are not sufficiently precise for detailed mechanistic analysis, the following conclusions and limits can be put forward. At the same $[\text{Cl}^-]$ values, the chloride anation proceeds more rapidly in weak acidic solutions than in strong acidic solutions. The notable amounts of hydroxo species in weak acidic solutions are invoked to explain this result. A previous work¹¹ has pointed out the strong trans effect of the hydroxide ligand to labilize the water ligand replaced by Cl^- .

Reactions 4 and 6 provide an acid-base catalytic pathway

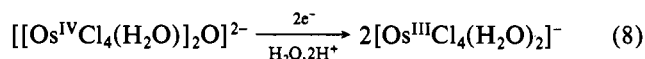


for substitution in the $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ complex as in reaction 7.

5. Redox Behavior of Aquochloroosmate(IV), $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})]_2\text{O}]^{2-}$. The μ -oxo-bridged dimer $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})]_2\text{O}]^{2-}$ is not reducible in aqueous chloride media at a platinum electrode but is reducible at a standard dropping-mercury electrode. The electronic transfer is likely associated with

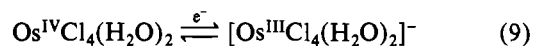
chemical reactions. A plot of $\log [(i_d - i)/i]$ vs. E from the current-potential curve does not give a straight line. The mechanism by which the dimer is reduced has not yet been investigated. However, it seems analogous to those reported previously⁵⁰ for the μ -oxo-bridged ruthenium dimer $[[\text{Ru}^{\text{IV}}\text{Cl}_5]_2\text{O}]^{4-}$. The exhaustive electrolysis of the dimer can be achieved very slowly at a platinum grid at a very cathodic potential ($E = -0.28$ V) (near the background discharge). Indeed when the Hg electrode is used, interference with mercury oxidation occurs. During the electrolysis, an anodic wave develops on the RDE voltammograms (Figure 9) and is concomitant with the decrease of the absorption at 370 nm (Figure 10). The $E_{1/2}$ and the limiting current of the voltammogram obtained on the resulting solution are analogous with those obtained at higher $[\text{Cl}^-]$ values.

The following conclusions can be put forward: the reduction of $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})]_2\text{O}]^{2-}$ occurs with simultaneous cleavage of the oxo bridge in the time scale of the CPE.



Besides, some deformations on the RDE voltammograms occurs in the anodic current with the appearance of a new minor wave at more anodic potential $E_{1/2} = +0.6$ V (1 M HCl), the major species being $[\text{Os}^{\text{III}}\text{Cl}_4(\text{H}_2\text{O})_2]^-$ with respect to the $E_{1/2}$ value.

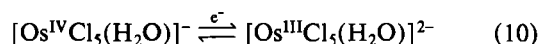
$\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$. The new species $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ is reducible at a platinum electrode. The CV and RDEV data are in good accordance with a quasi-reversible one-electron transfer with $\Delta E_p = 0.08$ V and $E_{1/2} = 0.19$ V (6.17 M HCl). Besides, $i_p/v^{1/2}$ gives a constant value consistent with a diffusion-controlled system. For $[\text{H}^+]$ greater than 6 M, the peak to peak separation is close to the theoretical value 0.06 V, representative of a Nernstian diffusion-controlled system. Departure from reversibility appears progressively on raising H_0 ³⁶ above -0.7 . Above -0.5 the hydroxo species is present in solution at equilibrium. However, the conversion of the hydroxo form to the aquo form is likely fast at a low H_0 value on the time scale of the CV, and the specific CV peak of the hydroxo form is not clearly observed, the aquo form being generally easier to reduce than the hydroxo form.⁵¹ Exhaustive electrolysis past the wave consumes 1 faraday/mol. Moreover on the time scale of the CPE, some deformations appear on the CV and RDE voltammograms particularly at a high $[\text{Cl}^-]$ value. The interpretation of the phenomenon is given below.



The $E_{1/2}$ value can be regarded as a good estimate⁵² for the formal reduction potential $E_0 = +0.19$ V (6 M HCl).

$[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ is reducible at a platinum electrode but is more difficult to reduce than $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$. The CV and RDEV data are in good accordance with a diffusion-controlled reversible one-electron transfer with $\Delta E_p = 0.07$ V and $E_{1/2} = +0.06$ V (11.7 M HCl).

The Os(IV)-Os(III) system is reversible in the experimental HCl range. However, a shift of the $E_{1/2}$ value is observed in less acidic media with $E_{1/2} = +0.10$ V (6 M HCl). Exhaustive electrolysis past the wave consumes 1 faraday/mol. Moreover on the time scale of the CPE, some deformations on the CV and RDE voltammograms appear particularly at high Cl^- values. The interpretation of the phenomenon is given below.



(50) L. W. Potts and H. S. Swofford, *Anal. Chem.*, **47**, 131 (1975).

(51) N. R. De Tacconi, D. Lexa, and J. M. Saveant, *J. Am. Chem. Soc.*, **101**, 467 (1979).

(52) H. E. Toma and C. Creutz, *Inorg. Chem.*, **16**, 545 (1977).

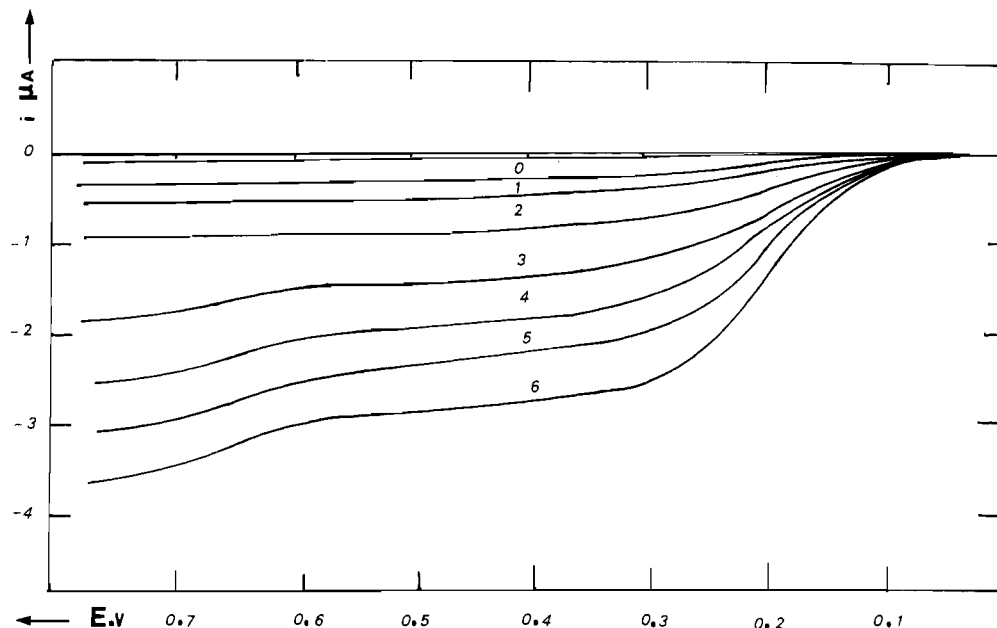


Figure 9. Rotating-disk-electrode voltammograms resulting from the exhaustive electrolysis at $E = -0.28$ V vs. SCE of the dimer $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})]_2\text{O}]^{2-}$ in 1 M HCl; $[\text{Os}] = 10^{-3}$ M.

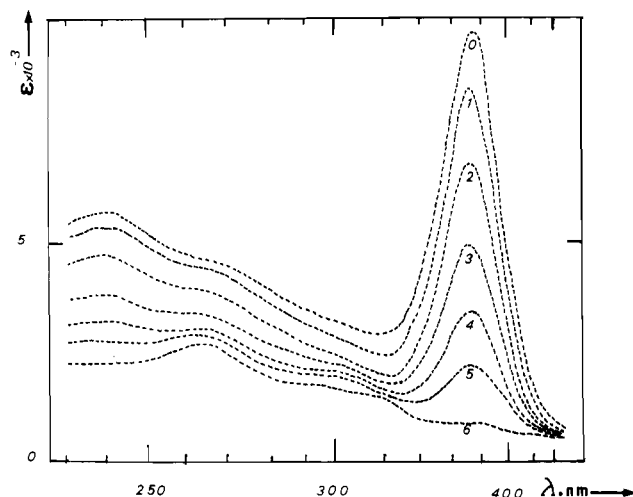


Figure 10. Spectral changes resulting from the exhaustive electrolysis at $E = -0.28$ V vs. SCE of the dimer $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})]_2\text{O}]^{2-}$ in 1 M HCl; $[\text{Os}] = 10^{-3}$ M.

The $E_{1/2}$ value can be regarded as an estimate for the formal reduction potential⁵² ($E_0 = +0.10$ V) (6 M HCl).

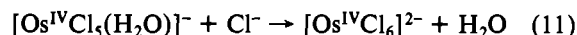
For comparison purposes, the redox behavior of $[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$ is investigated on a known sample in the experimental chloride media. $[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$ is more difficult to reduce than both $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ and $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$. The CV and RDEV data are consistent with a diffusion-controlled reversible one-electron transfer with $\Delta E_p = 0.07$ V and $E_{1/2} = -0.02$ V (11.7 M HCl). The Os(IV)–Os(III) system is reversible in the experimental HCl range. Nevertheless as it is observed for other Os(IV) species, the $E_{1/2}$ value shifts with changes of the supporting media ($E_{1/2} = +0.01$ V) (6 M HCl).

Exhaustive electrolysis past the wave consumes 1 faraday/mol. During the CPE, the $E_{1/2}$ and the limiting current values of the RDEV are approximately constant and characteristic of a reversible redox Os(IV)–Os(III) system without post associated chemical reaction. However, at low $[\text{Cl}^-]$ values some deformations are observed on the CV and RDEV of the reduced solutions. The interpretation of the phenomenon is given below.

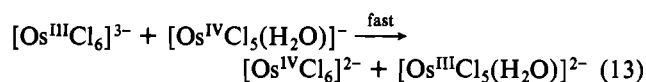
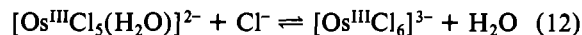
6. Chloride Anation of $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ and $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$. Redox Catalytic Pathways. $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ is stable in 11.7

M HCl at room temperature over several hours. The CPE past the reversible wave initiates spectral and electrochemical changes even at the Os(IV) rate. After the consumption of 0.04 faraday/mol, the transformation goes to completion over some minutes. The resulting solution is shown to be $[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$ by its spectral characteristics.

After the consumption of 0.01 faraday/mol, the chloride anation is slower and the course of the reaction can be followed by spectrophotometry, CV and/or RDEV. Spectral scans gave good isosbestic points in good agreement with those reported previously²⁹ for the chloride anation of $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ at 80 °C. The $E_{1/2}$ values shifts from +0.06 to -0.02 V. These results are in accordance with a redox catalysis^{53–58} of reaction 11. Reaction 11 is catalyzed by the Os(III) state. There are



several examples of such a redox catalysis in the literature.^{53–58} It involves both substitution on the catalyst species and electron transfer between the two oxidation degrees of the metal (eq 12 and 13).



Reactions 12 and 13 provide a catalytic pathway for reaction 10. The lability of reaction 11 is easily verified: $[\text{Os}^{\text{III}}\text{Cl}_6]^{3-}$ in 11.7 M HCl ($E_{1/2} = +0.01$ V) was introduced in 4 M HCl; over several minutes of aging a supplementary wave appears ($E_{1/2} = +0.11$ V) corresponding to $[\text{Os}^{\text{III}}\text{Cl}_5(\text{H}_2\text{O})]^{2-}$. Addition of concentrated HCl gives the single wave ($E_{1/2} = +0.01$ V) over several minutes. These qualitative results point out the lability of the Os(III) state compared to the Os(IV) state and state the validity of reaction 11. The rapidity of the electron transfer for the outer-sphere redox reaction (13) is

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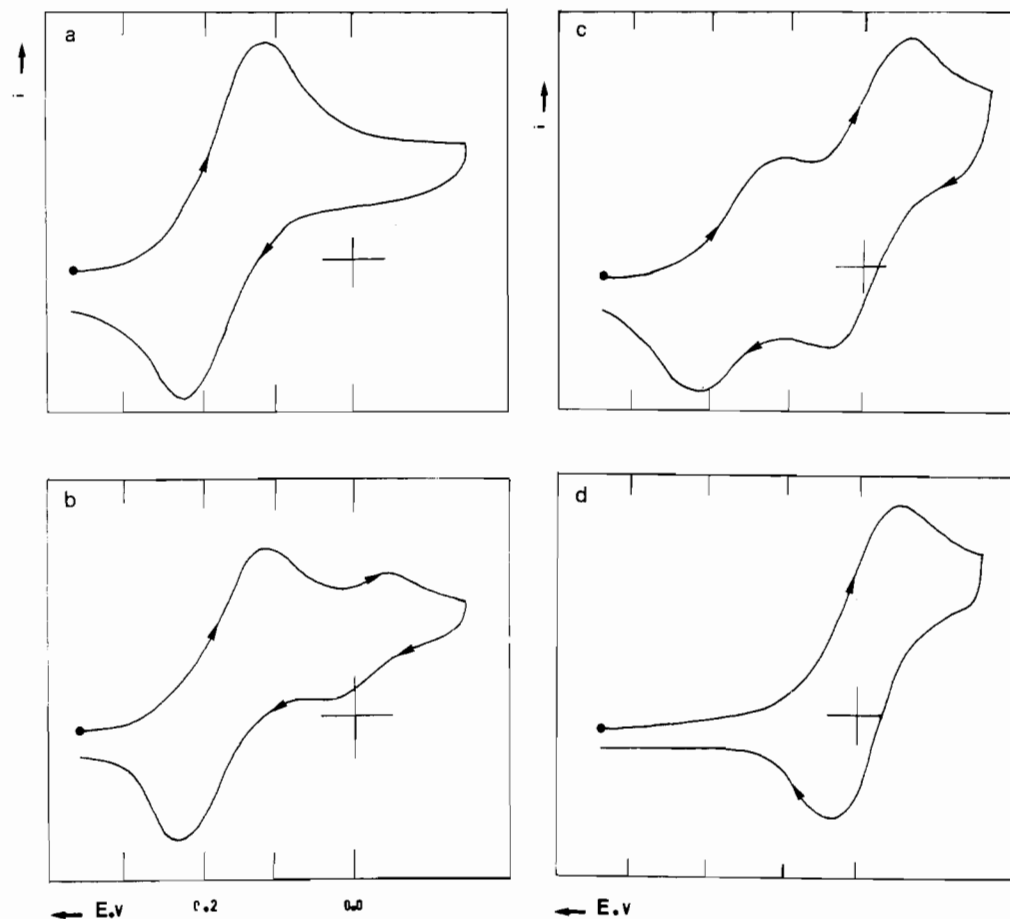


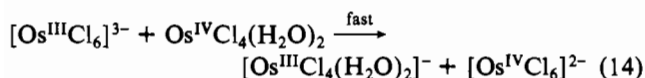
Figure 11. Cyclic voltammetric changes during the anation in 6 M HCl of $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2 + \text{Cl}^- \rightarrow [\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$ after addition of $[\text{Os}^{\text{III}}\text{Cl}_6]^{3-}$ (5%): a, CV of $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ generated by electrolysis of Os(VI); d, CV of $[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$.

checked qualitatively in 4 M HCl by rapidly mixing $[\text{Os}^{\text{III}}\text{Cl}_6]^{3-}$ ($E_{1/2} = 0.01$ V) and $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ ($E_{1/2} = 0.11$ V).

At the experimental $[\text{Cl}^-]$ value, the catalytic pathway and the aquation of $[\text{Os}^{\text{III}}\text{Cl}_6]^{3-}$ are supposed to be negligible on the time scale of the fast chemical redox reaction (13). The outer-sphere reaction (13) is thermodynamically favorable: $\log K_{13} = E_5^\circ - E_6^\circ/0.06$ and $K_{13} = (5 \pm 1) \times 10$ in 6.0 M HCl at 25 °C.

$\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ is stable in 6.0 M HCl at room temperature for over 1 h; then chloride anation occurs to give $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ (Figure 8). The CPE past the wave initiates supplementary spectral and electrochemical changes (Figure 11) at the Os(IV) state. After the consumption of 0.05 faraday/mol, the transformation goes to completion in 6.0 M HCl at room temperature. The resulting solution is shown to be $[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$. $E_{1/2}$ shifts from +0.19 to +0.01 V. These results are in accordance with a redox catalysis of the substitution reactions 6 and 10. These are catalyzed by the Os(III) state.

The rapidity of the electron transfer for the outer-sphere redox reaction of (14) is checked qualitatively in 4 M HCl by rapidly mixing $[\text{Os}^{\text{III}}\text{Cl}_6]^{3-}$ ($E_{1/2} = 0.01$ V) and $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ ($E_{1/2} = 0.19$ V).

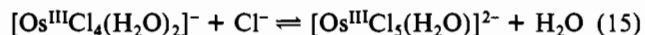


At the experimental $[\text{Cl}^-]$ value, the catalytic pathway and the aquation of $[\text{Os}^{\text{III}}\text{Cl}_6]^{3-}$ are negligible in time scale of the fast chemical redox reaction of (14). The outer-sphere reaction of (14) is thermodynamically favorable, with $\log K_{14} = E_4^\circ - E_6^\circ/0.06$ and $K_{14} = (10 \pm 2) \times 10^2$ at 25 °C in 6.0 M HCl. No experimental evidence for the $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ species is

Table III. Number of Chloroosmate(III) Species of the Resulting Solutions of the Electrochemical Reduction of Os(IV) Species

$[\text{Cl}^-]$, M	$[\text{H}^+]$, M	r (σ)	P
1.09–11.07	0.4–11.7	4 (0.01)	4
1.09–3.3	1.09–3.3	2 (0.01)	2
4.45–11.7	4.45–11.7	2 (0.01)	2
8.25–11.7	8.25–11.7	1 (0.01)	1

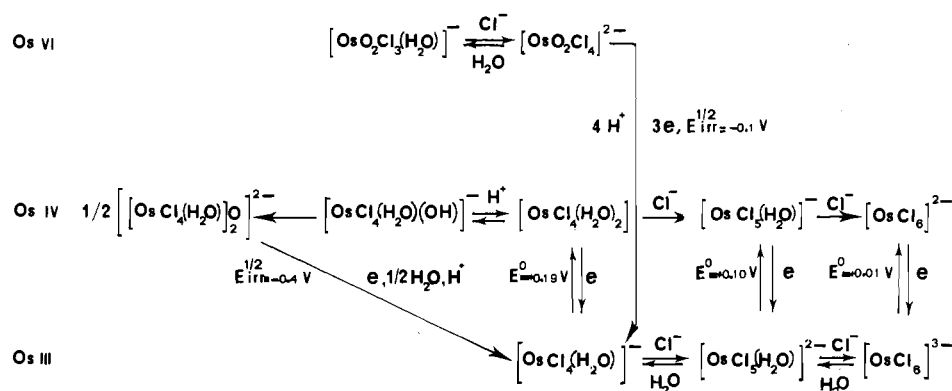
observed in the chloride anation catalytic pathway. Reactions 12, 14, and 15 provide a catalytic pathway for reactions 7 and 11.



7. The Os(III) Species. Number and Properties. The rank-matrix analysis of spectrophotometric data of chloride solutions obtained after exhaustive electrolysis detects four Os(III) species (Table III) over the experimental $[\text{H}^+]$ and $[\text{Cl}^-]$ ranges. For aquo complexes a decrease of the oxidation of the metal is associated with a higher value of pK_A ; consequently deprotonation does not occur in the Os(III) state in the experimental $[\text{H}^+]$ range. The Os(III) species number is in good accordance with the electrochemical experiments. The composition of the Os(III) species is given in keeping with the corresponding Os(IV) species composition: $[\text{Os}^{\text{III}}\text{Cl}_6]^{3-}$, $[\text{Os}^{\text{III}}\text{Cl}_5(\text{H}_2\text{O})]^{2-}$, $[\text{Os}^{\text{III}}\text{Cl}_4(\text{H}_2\text{O})_2]^-$. It is not possible with the present experimental data to formulate the supplementary species generated by the CPE of the dimer $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2]_2\text{O}]^{2-}$ in 1 M HCl ($E_{1/2} = +0.6$ V).

The examination of the data listed on Table III reveals that for $[\text{Cl}^-]$ greater than 4.45 M two species $[\text{Os}^{\text{III}}\text{Cl}_6]^{3-}$ and $[\text{Os}^{\text{III}}\text{Cl}_5(\text{H}_2\text{O})]^{2-}$ make major contributions to solution composition while below 3.3 M Cl^- the major species are $[\text{Os}^{\text{III}}\text{Cl}_4(\text{H}_2\text{O})_2]^-$ and the unformulated Os(III) species.

Scheme I



The CPE past the different anodic waves generates the expected monomeric Os(IV) species. In the case of mixtures, instead of oxidizing Os(III) in a single step at say +0.6 V it is possible to oxidize in several stages the Os(III) species past the respective oxidation waves: the inertness^{46,47} to substitution reactions in the Os(IV) state does not allow post associated chemical reactions. However, at low [HCl] values spectral and electrochemical changes are observed in the Os(IV) state after CPE. The limiting current of the RDEV decreases progressively. This feature is in good accordance with the slow olation reaction of (5) (vide supra).

The Os(III) species are also chemically oxidized by the dioxoosmate(VI) species; these reactions are used as corroborative evidence for the overall reduction mechanism of dioxoosmate(VI) species.

When chloride solutions of Os(III) and Os(VI) species are mixed, Os(IV) solutions are generated. Indeed the spectral and electrochemical characteristics of Os(IV) species are detected. The stoichiometry^{27c} of reaction 2 is derived from a spectrophotometric titration ($2\text{Os}^{\text{III}} + \text{Os}^{\text{VI}} \rightarrow 3\text{Os}^{\text{IV}}$).

The chemical redox reaction is fast over the experimental $[\text{H}^+]$ range, and the associated reactions such as anation or olation are negligible on the time scale of the redox reaction. In 1 M HCl, when the Os(III) species (the major species being $[\text{Os}^{\text{III}}\text{Cl}_4(\text{H}_2\text{O})_2]^-$) are rapidly mixed with $[\text{Os}^{\text{VI}}\text{O}_2\text{Cl}_4]^{2-}$, $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ and its deprotonated form are predominantly generated (see eq 2).

At higher HCl values, the resulting Os(IV) solution is a mixture of three species: $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$, $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$, and $[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$ as evidenced by the spectral and electrochemical experiments.^{27c}

Discussion

Scheme I gives a summary of the overall electrochemical behavior of the various forms and oxidation states of chloroosmates examined in this study. From the results obtained in chloride media in the experimental range 1–8.25 M, it is now possible to give a good interpretation of the electroreduction of oxoosmate(VI) species in these media. Os(VI) undergoes a very irreversible electronic transfer through $[\text{Os}^{\text{VI}}\text{O}_2\text{Cl}_4]^{2-}$, which proceeds by a single three-electron step to give directly $[\text{Os}^{\text{III}}\text{Cl}_4(\text{H}_2\text{O})_2]^-$. The electron transfer is coupled with proton transfers. The rate of reduction is limited by the chemical conversion shown in eq 1. A fast post associated chemical redox reaction occurs between $[\text{Os}^{\text{III}}\text{Cl}_4(\text{H}_2\text{O})_2]^-$ and $[\text{Os}^{\text{VI}}\text{O}_2\text{Cl}_4]^{2-}$ to give $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$. This latter species is more easily reducible than the starting material and provides an autocatalytic pathway for the overall reduction of oxoosmate(VI) species. The electrode phenomena are in good accordance with the results observed during exhaustive electrolysis. However, on the time scale of the CPE, the dimeric species $[[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2]_2\text{O}]^{2-}$ is generated at low

[HCl] values. This species is less easily reducible than the starting material. Nevertheless no structural evidence have been obtained for the oxo bridge in previous and present works. The reduction mechanism of the dimer have not been investigated yet but is presumably analogous to those reported for $[[\text{RuCl}_5]_2\text{O}]^{4-}$ with cleavage of the oxo bridge. It should be noted that the known^{59,60} $[[\text{OsCl}_5]_2\text{O}]^{4-}$ is not detected in the experimental conditions.

The inertness to substitution reactions of chloroosmates in the Os(IV) state allows to obtain several species in solution by electrochemical means: $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$, $[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$, and $[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$. Unfortunately, attempts to isolate the aquochloro complexes are unsuccessful as of yet. The kinetic stability of the complexes increases with the chloride number. However, several catalytic pathways accelerate the chloride anation reactions: acid–base catalysis through hydroxo Os(IV) species and redox catalysis through Os(III) species.

The charge-transfer absorptions observed for the Os(III) and Os(IV) chloro complexes are described as arising through electron transfer from a ligand orbital to a metal d orbital.^{61,62} Upon reduction of the control metal–Os(IV), the receptor orbital becomes less stable and the CT absorptions are shifted to higher energy (Os(III)).

The electrochemical data presented in Scheme I reveal several trends in the stabilization of osmium(IV) centers by chloride ligands. The number of halides present figures in the reduction of Os(IV)/Os(III) couples. Each coordinated water replaced by a chloride lowers the reduction potential by approximately 90 mV. Comparable behaviors are observed for Os(IV)–ammines⁶³ and are expected on the basis that the chloride ligands are negatively charged and act as π -electron donors.

The highly acidic nature of the aquochloroosmate(IV) species is not unexpected. The low $\text{p}K_a$ values may be attributed to the high oxidation state of the central metal and to high electron affinity of the $d^4 t_{2g}$ orbitals which stabilizes the hydroxo ligand formed on deprotonation. An increase in the number of chlorides is expected to decrease the coordinated water first acidity because of the decreased overall charge of the complex. Theoretically, configurational differences also control stabilization provided by the chloride ligands. Without structural experiments, it is not possible to assign the trans or cis geometry to $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$. However, the electrochemical properties are characteristic of a single species; be-

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sides, the Os(IV) species derives from $[\text{Os}^{\text{VI}}\text{O}_2\text{Cl}_4]^{2-}$ with the trans dioxo moiety $\text{O}=\text{Os}=\text{O}$. It is probable that the reduction occurs with retention of trans configuration in the Os(IV) state, which is inert. Nevertheless it is possible that isomerization occurs in the Os(III) state.

Registry No. $[\text{Os}^{\text{VI}}\text{O}_2\text{Cl}_4]^{2-}$, 39162-54-4; $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$, 67378-38-5; $[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2\text{O}]^{2-}$, 74355-72-9; $[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$, 16871-52-6;

$[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$, 59683-36-2; $[\text{Os}^{\text{III}}\text{Cl}_4(\text{H}_2\text{O})_2]^-$, 80642-48-4; $[\text{Os}^{\text{III}}\text{Cl}_5(\text{H}_2\text{O})]^{2-}$, 74009-23-7; $[\text{Os}^{\text{III}}\text{Cl}_6]^{3-}$, 62792-05-6; $[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})(\text{OH})]^-$, 80695-88-1; $[\text{Os}^{\text{IV}}\text{Cl}_4(\text{OH})_2]^{2-}$, 20617-39-4.

Supplementary Material Available: Calculations of $\text{p}K_1$ and $\text{p}K_2$ values and of resolved UV-vis spectra and a listing of observed and calculated absorbances obtained during the deprotonation of $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ (5 pages). Ordering information is given on any current masthead page.

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Water Exchange and Solvolysis in Dimethyl Sulfoxide of Square-Planar Tetraaquaplatinum(II). A Platinum-195 NMR Study

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Isotopic shifts of -1.00 , -0.81 , and -0.63 ppm have been observed for the platinum-195 NMR signals from the complexes $\text{Pt}(\text{H}_2\text{O})_4^{2+}$, *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$, and *trans*- $\text{PtCl}_2(\text{OH})_2^{2-}$, respectively, when an ^{16}O ligand is exchanged for ^{18}O . The resolved isotopic shifts indicate that there are four equivalent slow-exchanging aqua ligands in the hydrated platinum(II) ion, corresponding to a coordination number of 4. Axial interaction of fast-exchanging water is probably not very significant. The exchange frequency for $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ at 25 °C is $2.3 \times 10^{-3} \text{ s}^{-1}$, corresponding to a second-order rate constant for water exchange of $4.5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. The activation parameters are $\Delta H^\ddagger = 100 \pm 10 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 40 \pm 30 \text{ J mol}^{-1} \text{ K}^{-1}$. ^{195}Pt spin-lattice relaxation in $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ is mainly due to chemical shift anisotropy. Solvolysis of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ in dimethyl sulfoxide solvent has been studied with use of UV spectrophotometry. The rate constant at 25 °C for the substitution of the first aqua ligand by Me_2SO is $1.1 \times 10^{-3} \text{ s}^{-1}$, and the activation parameters are $\Delta H^\ddagger = 90 \pm 1.5 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 2 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$. The kinetic parameters for the water exchange and the dimethyl sulfoxide solvolysis of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ indicate that the mechanism for these two reactions is mainly dissociative. In combination with previous kinetic data for the reaction of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ with various entering ligands X it is thus likely that there is a gradual change of mechanism from mainly dissociative to mainly associative when the ligands X are changed in the order H_2O , Me_2SO , Cl^- , Br^- , I^- .

Introduction

No studies of water exchange of square-planar platinum(II) aqua complexes have been reported so far. A number of paramagnetic metal ions with labile water in the inner coordination sphere have been investigated with use of the effect of the paramagnetic metal ion on the line width of the ^{17}O NMR resonance.^{1,2} For metal ions with a relatively inert coordination sphere, on the other hand, there is no generally applicable method to monitor the water exchange. For a few systems of Co(III), Cr(III), Rh(III), and Ir(III), precipitation of sparingly soluble salts followed by mass spectrometric analysis has been used to follow the exchange of inner-sphere H_2^{16}O for bulk H_2^{18}O .³ This method has also been used to monitor exchange between oxo anions and solvent water.⁴ It will probably not be possible to find a precipitating agent for the platinum(II) aqua complexes that does not interfere with the exchange.

Platinum-195 chemical shifts are very sensitive to the environment of the platinum.⁵⁻⁹ Oxygen isotope effects like

those reported¹⁰ for the ^{55}Mn and ^{95}Mo resonances from the complexes MnO_4^- and MoO_4^- should therefore be expected in the chemical shifts of platinum coordinated to oxygen. The present study shows that such oxygen isotope effects exist and can be utilized to determine both the coordination number of $\text{Pt}(\text{aq})^{2+}$ and the rate and activation parameters for the water exchange of platinum(II) aqua species. In this context, a determination of the activation parameters for the solvolysis of tetraaquaplatinum(II) in dimethyl sulfoxide will also be reported.

Experimental Section

Chemicals and Solutions. A solution of tetraaquaplatinum(II) perchlorate (15.1 mM) in perchloric acid (1.00 M; Baker p.a.) was prepared from potassium tetrachloroplatinate(II) (Johnson and Matthey) and anhydrous silver perchlorate (F. Smith) as described previously.¹¹ The solution was concentrated to $C_{\text{Pt}} = 44.2 \text{ mM}$ and $C_{\text{HClO}_4} = 2.85 \text{ M}$ by freezing out water at -18 °C. The UV spectrum of the concentrated solution was identical with the spectrum of $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ reported previously,¹¹ and its platinum concentration was determined spectrophotometrically at 273 nm ($\epsilon = 56.5 \text{ cm}^{-1} \text{ M}^{-1}$). The molarity of H_2^{16}O was calculated from the concentrations and the density of the solution (1.1787 g cm^{-3}) to be $87.5 \pm 0.2\%$ relative to pure water. The original concentration of potassium from K_2PtCl_4 is reduced somewhat in the final solution because some solid potassium perchlorate is also precipitated during the freezing out of water. This is negligible for the determination of the water molarity.

A 44.2 mM solution of *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ was prepared by adding solid sodium chloride (to give 0.2 M) to the 44.2 mM tetraaquaplatinum(II) solution and aging for 1 h at room temperature. According to the chloride anation rate constants for $\text{Pt}(\text{H}_2\text{O})_4^{2+}$, $\text{PtCl}(\text{H}_2\text{O})_3^+$, and *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$,¹² the *trans* complex is accumulated to almost 100% within this time and remains unchanged for several hours. This was confirmed by a constant intensity of the

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