electrode was performed with a Princeton Applied Research Model 173 potentiostat equipped with a Model 176 current-to-voltage converter. Cyclic voltammetric curves were either displayed on a Tetronix 5115 storage oscilloscope or recorded on a Houston Series 2000 x-y recorder. Polarographic and microvoltammetric results were recorded directly on the x-y recorder. Pollution of the electrodes was not apparent in these studies. Aging of the solution was also undetected under these conditions, since we were able to reproduce the potential/current profiles throughout the course of an experiment. The platinum-disk working electrode was periodically polished with a very fine emery cloth.

The cyclic voltammetric and microvoltammetric cell were of airtight design with high-vacuum Teflon valves (Kontes) and Viton O-ring seals to allow an inert atmosphere to be maintained without contamination by grease. The adjustable platinum working electrode was imbedded in a cobalt glass seal to allow periodic polishing without significantly changing the surface area. The SCE reference and saturated KCl salt bridge were separated from the solution by a cracked glass tip. The counter electrode, consisting of a platinum gauze was separated from the working electrode by less than 2 mm and was connected to the reference electrode via a 0.1-μF capacitor to aid in the compensation for *iR* drop.

The standard oxidation and/or reduction potentials for the tetracobalt clusters determined by cyclic voltammetry were evaluated from the anodic ($E_p{}^a$) and cathodic ($E_p{}^c$) peak potentials (when permitted).[27] The $E_{1/2}$ values from microvoltammetric and polarographic analyses were obtained from the magnitude of the limiting-current and applied-potential curves.

Instrumentation. IR spectra were recorded on either a Perkin-Elmer 467 and 298 spectrometer as liquid solutions in 1.0-mm chloride cells. All IR spectra were calibrated against the 1601-cm^{-1} band of a polystyrene film. UV–vis spectra were recorded on a Hewlett-Packard 8450A diode array spectrophotometer.

Electrocatalysis of Ligand Substitution. Typical Procedure. To an argon-flushed electrolysis cell was added ~0.03 g (~0.0355 mmol) of $Co_4(CO)_{10}(PPh)_2$, followed by 5–7 mL of solvent containing 0.1 M TBAP. The desired amount of the phosphorus(III) nucleophile such as PPh_3 was added to the stirred solution. The electrocatalytic reaction was initiated by passage of ~2.0 mA of cathodic current in the constant-current mode. The initial potential of −1.0 V rose to −1.15 V as the substitution reaction proceeded. The extent of the substitution reaction was monitored by IR spectrophotometry after the passage of 6% of the theoretical charge required for the moles of $Co_4(CO)_{10}(PPh)_2$ charged. The yield of $Co_4(CO)_9(PPh)_2PPh_3$ was determined by monitoring the absorbance of the 2060-cm^{-1} stretching band of the monosubstituted cluster. In desired cases, the monosubstituted cluster was isolated by column chromatography, and it was shown to be identical with an authentic sample prepared independently. In no case was there any evidence for the disubstituted cluster under these conditions.

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Ruthenium(III) Chloride in Aqueous Solution: Electrochemical and Spectral Studies

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Chloro complexes of ruthenium(III) in 0.1 M KCl at pH 0.4, 1.0, and 2.0 and temperature 25 °C have been investigated with use of electrochemical and spectrophotometric techniques. The species characterized in solution are $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$, and $[RuCl(H_2O)_5]^{2+}$. The equilibrium constants for the formation of these species are reported at 25 °C (μ = 0.1 M KCl). The reduction potentials and the characteristic charge-transfer bands for these ions have also been reported. The electrochemical and spectral behaviors of a solution containing these species were found to change with time, which was explained in terms of the various solution equilibria and stabilities of the species in solution. The species $[RuCl_2(H_2O)_4]^+$ was found to be the most stable present in solution under these experimental conditions. The species $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, and $[RuCl(H_2O)_5]^{2+}$ are converted to the more stable $[RuCl_2(H_2O)_4]^+$ species as evidenced from time-drive absorption spectra. These conversions are found to be fast in solutions heated to temperatures higher than 70 °C at pH 2.0 with the concomitant hydrolysis of the metal ion.

Introduction

Ruthenium and its chloro complexes particularly in the +3 oxidation state have evinced a great deal of interest in recent years because of their use in homogeneous catalysis.[1-10] Ruthenium(III) chloride and its EDTA complexes have recently been successfully employed as catalysts in the oxidation of allyl alcohol, ascorbic acid, and cyclohexanol.[3-6] The spectral behavior and solution stabilities of ruthenium(III) and its chloro complexes, however, have not yet been studied in detail.

Ruthenium(III) forms a variety of chloro complexes of the type $[MX_mY_n]^{(m-n-3)-}$ (where M = Ru^{3+}, X = Cl^-, Y = H_2O, m = 1–6, n = 0–5, and $m + n$ = 6). The hexa- and pentachloro complexes are isolable[11-13] from concentrated hydrochloric acid (>6 M) solution, but the other species, though known in solution, could not be isolated. The variation of color intensity of ruthenium(III) solution with its concentration[14,15] in hydrochloric acid also supports the existence of several equilibria in solution. Since anionic chloro complexes of ruthenium(III) are substitution labile and equilibrate rapidly in solution,[16] the composition of each complex species under equilibrium in solution is largely affected by hydrochloric acid concentration. Connick et al.[16,17] determined the charge per species of the chloro complexes by ion-exchange elution

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methods. The existence of the various chloro species in solution[16-18] and the equilibrium constants for their formation[19-21] were reported. The hydrolytic tendency of ruthenium(III) in perchloric acid medium up to 1-6 M was attributed[22,23] to the formation of $[Ru_2(OH)_2]^{4+}$ in solution.

Because of the limited data on the nature of ruthenium(III) chloro species in solution, few attempts were made to investigate their electrochemical behavior.[24-26]

The present paper deals with the investigation of chloro complexes of ruthenium(III) at a dropping mercury electrode using millimolar solutions in the pH range 0-2.0. Differential pulse polarograms were also taken for the experimental solutions containing different ruthenium(III)-chloro complexes. The limiting currents for these species were found to change with time, pH, and depolarizer concentration, indicating the decay, polymerization, and hydrolysis of these ions. The results were confirmed by coulometry. The nature of these species in solution was simultaneously followed by spectrophotometric measurements, and the equilibrium constants were calculated.

Experimental Section

Materials and Methods. Stock solution of ruthenium(III) (10 mM) was prepared in 1 M hydrochloric acid by dissolving the appropriate amount of ruthenium trichloride ($RuCl_3 \cdot 3H_2O$) obtained from Johnson Matthey Inc. The solution thus prepared was allowed to stand at room temperature for 3-4 days, allowing for the monomeric chloro complexes[11] to reach equilibrium. The solution so found is reddish brown with a yellow tinge. The ruthenium content in these solutions (10 mM) was determined by a known spectrophotometric method using thiourea.[27] The ruthenium concentration in these solutions was determined from the absorbance at 620 nm with a molar extinction coefficient of 2.47×10^3 M^{-1} cm^{-1}. The values were also checked with those of a standard ruthenium(III) solution (AAS) supplied by Aldrich Chemical Co. Experimental solutions were made by pipetting appropriate amounts of ruthenium solution into 10 mL of 0.1 M potassium chloride solution. A pH of 0.4-2.0 was adjusted in the solution with use of 1 M hydrochloric acid and 0.1 M sodium hydroxide solutions. The possibility of oxidation of ruthenium(III) in hydrochloric acid[16] was checked by an oxygen absorption method using a manometric setup. There was no absorption of O_2 by ruthenium(III) solution; thus the formation of ruthenium(IV) by aerial oxidation was excluded. The solution was also tested with potassium iodide solution to detect the presence of any ruthenium(IV) in the stock solution. All the chemicals used were of analytical grade, and the solutions were prepared with use of double-distilled water.

Physical Measurements. All pH measurements were made with a Digisun Model DI-707 pH meter readable to 0.01 pH. The absorption spectra were recorded on a Beckman Model DU-7 high-speed UV/vis spectrophotometer. The electrochemical measurements were made with Princeton Applied Research (PAR) electrochemical instruments equipped with a high-precision X-Y recorder. Dc and differential pulse polarography measurements were done by the use of a PAR 174A polarographic analyzer keeping the scan speed (v) at 2 mV/s. The three-electrode measurements were carried out with a PAR 303 SMDE assembly provided with a DME/HMDE as the working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl reference electrode. The static mercury drop electrode used in this work had an average drop mass of 2.75 mg in 0.1 M KCl with an open circuit and a drop time of 2 s. Controlled-potential coulometry was performed by using a PAR 173 potentiostat, a PAR 179 digital coulometer, and a PAR 377A cell system taking a mercury pool as a working electrode. All the electrochemical studies were made after purging purified nitrogen gas through the experimental solutions maintained at 25 °C.

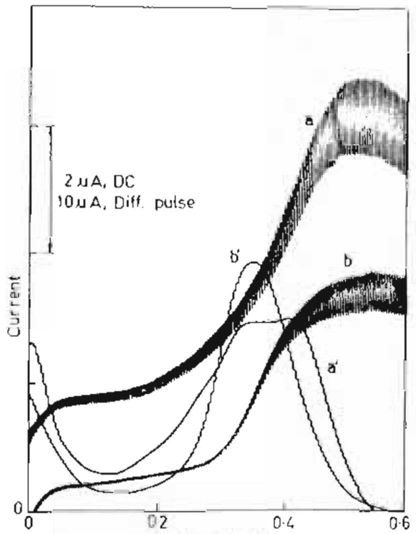

Figure 1. Dc and differential pulse polarograms of ruthenium(III) (mM) at pH 1.0 (μ = 0.1 M (KCl), t = 25 °C): (a,a′) immediately after preparation; (b,b′) after 24 h.

Results and Discussion

Polarography. When millimolar solutions of ruthenium(III) in 0.1 M KCl were polarographically reduced at a DME, a polarogram in the potential range between −0.10 and −0.60 V was obtained. The behavior of this polarogram is highly dependent on two factors: the pH and the recording time after preparation of the solution. Polarograms a and b in Figure 1 for ruthenium(III) solutions at pH 1.0 in 0.1 M KCl illustrate the nature of polarographic changes that take place with time. The major observable changes are in the residual currents, the drop currents, and the wave formations. The polarogram of a freshly prepared solution of ruthenium(III) (Figure 1a) starts with a large residual current and has a plateau passing over a range of potentials from −0.10 to −0.50 V and a maximum on the limiting currents. This wave by its shape as well as by the nature of the logarithmic plots and k°_{fh} can be taken as ill-defined and irreversible.[28] The polarogram (Figure 1b) recorded after 24 h shows less residual currents and develops to a well-defined wave with the absence of a maximum. In this case the logarithmic plots and k°_{fh} values show the electrode reaction to be quasi-reversible. Both the polarograms are, however, found to be diffusion controlled. After 24 h there is a gradual decrease in the limiting current and an elongation of the plateau (Figure 1b) to more negative potentials. The millimolar solution of ruthenium(III) chloride in dilute hydrochloric acid, when stored beyond 150 days, does not show any electrochemical reductions between these potentials at the DME.

The solution of ruthenium(III) chloride at pH 0.4 shows almost the same electrochemical behavior as Figure 1a except for a pronounced maximum and enhanced irreversibility at the instant of preparation. As compared to the results at pH 1.0, a well-defined wave develops a little later and diminishes slowly with time. The solution at pH 2.0, however, gives a well-defined polarogram within $^1/_2$ h as seen in Figure 1b and becomes nonreducible in about 70 days.

It may be observed from Figure 1a that the polarogram may be the resultant of two or more closely separated waves for different reducible species in a nonequilibrium condition. These polarographic reductions in Figure 1a may be attributed[24-26,29] to one-electron reduction of the Ru(III)/Ru(II) couple involving the most plausible ruthenium(III) species like $[Ru(H_2O)_6]^{3+}$, $[RuCl(H_2O)_5]^{2+}$, $[RuCl_2(H_2O)_4]^+$, $[RuCl_3(H_2O)_3]$, $[RuCl_4(H_2O)_2]^-$, $[RuCl_5(H_2O)]^{2-}$, and $[RuCl_6]^{3-}$ ions. The aquo ion $[Ru(H_2O)_6]^{3+}$ is, however, unstable and may either complex with

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Table I. Peak Potentials Observed for Ruthenium(III) Solutions in Hydrochloric Acid at Different Time Intervals[a]

		peak potentials, V vs. Ag/AgCl (i_p, μA)				
pH	time/24 h	$-E_{p1}$	$-E_{p2}$	$-E_{p3}$	E_{p4}	$-E_{p5}$
0.4	0	0.255 (6.8)	...	0.360 (4.8)	0.455 (3.0)	...
	1	0.255 (6.5)	...	0.360 (11.5)	0.455 (s)	...
	2	0.255 (6.0)	...	0.360 (11.5)	0.455 (s)	...
	6	0.255 (3.3)	...	0.360 (13.3)	...	...
	13	0.255 (5.0)	...	0.370 (16.5)	...	...
	35	0.295 (5.5)	...	0.400 (16.0)	...	...
1.0	0	0.180 (1.7)	0.270 (5.0)	0.355 (5.5)	0.415 (1.5)	...
	1	...	...	0.350 (18.5)	...	...
	2	...	...	0.355 (18.5)	...	...
	3	...	...	0.355 (15.8)	...	...
	18	...	...	0.355 (8.3)	...	...
	21	0.240 (s)	...	0.360 (6.5)	...	...
	43	0.240 (s)	...	0.370 (3.1)	...	...
	105	0.290	...	...	...	0.530 (2.5)
2.0	0	...	...	0.365 (11.5)	...	...
	1	...	...	0.365 (8.7)	...	0.550 (1.0)
	4	...	...	0.365 (9.0)	...	0.550 (1.5)
	8	...	...	0.370 (10.0)	...	0.550 (3.0)
	15	0.240 (0.8)	...	0.370 (4.0)	...	0.550 (6.8)
	40	0.240 (0.5)	...	0.370 (2.8)	...	0.550 (7.5)
	102	0.300 (1.0)	...	...	...	0.550 (7.5)

[a] s = shoulder.

chloride ions or undergo extensive hydrolysis.[22,23] The hexa- and pentachloro complexes[11,12] that exist predominantly in a 6 M solution of hydrochloric acid are insignificant at pH 1.0. Thus the polarogram in Figure 1a is mainly due to one-electron reduction of each one of the $[RuCl(H_2O)_5]^{2+}$, $[RuCl_2(H_2O)_4]^+$, $[RuCl_3(H_2O)_3]$, and $[RuCl_4(H_2O)_2]^-$ species (confirmed in the later part of this paper) in nonequilibrium. The development of nonreducible character in these solutions (Figure 1b) may be attributed to the polymerization of the stable species through chloro or hydroxo bridges.[15,22,23]

The polarogram in Figure 1b is due to reduction of the most stable and dominating species $[RuCl_2(H_2O)_4]^+$ in equilibrium with other species in solution. Since all these species are reduced in closely separated overlapping steps, it is very difficult to evaluate the reduction potentials from the polarogram in Figure 1a. Buckley and Mercer[24] had, however, estimated approximate reduction potentials from polarography for the $[Ru(H_2O)_6]^{3+}$/$[Ru(H_2O)_6]^{2+}$, $[RuCl_2(H_2O)_4]^+$/$[RuCl_2(H_2O)_4]$, $[RuCl_3(H_2O)_3]$/$[RuCl_3(H_2O)_3]^-$, and $[RuCl_6]^{3-}$/$[RuCl_6]^{4-}$ couples by isolating each species[16,17] by an ion-exchange elution method.

In addition to a Ru(III)/Ru(II) reduction wave (Figure 1), there also appears a catalytic wave with large cathodic currents at potentials more negative than −0.60 V which corresponds to the catalytic decomposition of hydrogen ions at the mercury electrode.[30-32] The behavior of this catalytic wave does not change even after the polymerization of metal ion with aging of the solution. The cathodic limiting currents observed around 0.0 V as shown in Figure 1a,b are due to large anodic currents beyond this potential. These anodic currents are probably due to ruthenium(III) ion catalyzed oxidation of Hg by the chloride ions.

Differential Pulse Polarography. In order to substantiate the polarographic results and the solution stabilities of ruthenium(III) chloro species, the differential pulse polarographic technique was used. Figure 2 and 3 show the differential pulse polarograms recorded at different times for ruthenium(III) solutions at pH 0.4 and 2.0, respectively.

An instantly prepared solution of ruthenium(III) chloride at pH 0.4 gives three differential pulse polarographic maximum (Figure 2a) at E_p's($E_{1/2}$'s) −0.255, −0.360, and −0.455 V. As time proceeds, the peak at −0.455 V becomes a shoulder-type curve on the descending region and finally disappears completely after 6 days, while the peak at −0.360 V shows a steep increase in 24 h and attains symmetry in 6 days and a steady state in 13 days. However, a slow decrease in its peak height and a shift to −0.400 V were found beyond 13 days. The peak height at −0.255 V decreases gradually and finally becomes a shoulder on the rising curve after 3 days; thereafter a small potential shift after 35 days is observed.

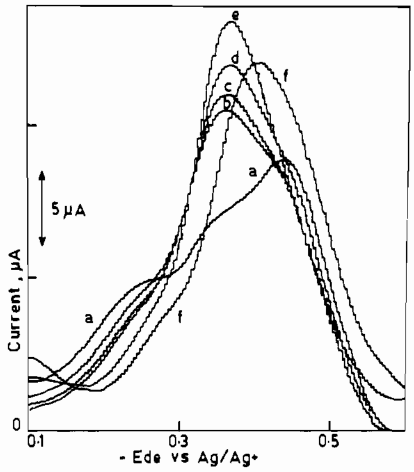

Figure 2. Differential pulse polarograms of pH 0.4 ruthenium(III) (mM) solution at different time intervals (h) (μ = 0.1 M (KCl), t = 25 °C): (a) 0; (b) 24; (c) 48; (d) 72; (e) 312; (f) 840.

The differential pulse polarograms at pH 1.0 recorded at the instant of preparation and after 24 h are shown in Figure 1a′,b′. It is evident from these polarograms that there are four different species in solution with reduction potentials at −0.180, −0.270, −0.350, and −0.415 V. The peak heights of the first, second, and fourth reduction steps diminish after 24 h. The third peak increases steeply and then decreases with time with a simultaneous shift in its potential to −0.370 V after 20 days. It disappears after about 100 days, and a new peak appears at −0.530 V.

The solution at pH 2.0 gives a single differential peak (Figure 3a), indicating a single species at −0.365 V. The peak height of this differential pulse polarogram steadily decreases with time with the appearance of a new peak at −0.550 V after 24 h. This peak attains a maximum height in 40 days. After 100 days a small peak appears around −0.300 V with no change in the peak at −0.550 V and no reduction peak at −0.365 V.

The results obtained at different pH and time are summarized in Table I. From these results it can be concluded that, at the instant of preparation, ruthenium(III) exists in solution in the pH

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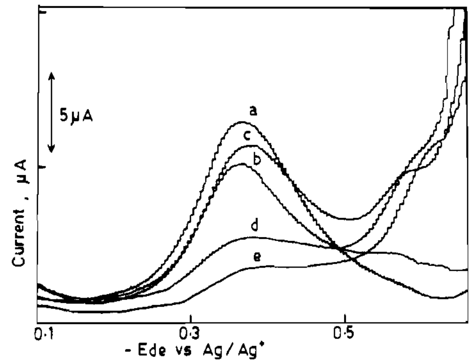

Figure 3. Differential pulse polarograms of pH 2.0 ruthenium(III) (mM) solution at different time intervals (h) (μ = 0.1 M (KCl), t = 25 °C): (a) 0; (b) 24; (c) 192; (d) 360; (e) 600.

Table II. Approximate Percentages of Different Ruthenium(III)–Chloro Complexes in Instantly Prepared Solutions at Different pHs

species	pH 0.4	pH 1.0	pH 2.0
$[RuCl_4(H_2O)_2]^-$	47.4[a]	12.1	...
$[RuCl_3(H_2O)_3]$		36.6	...
$[RuCl_2(H_2O)_4]^+$	31.6	40.3	100
$[RuCl(H_2O)5]^{2+}$	21.0	11.0	...

[a] Sum of the first two species.

range 0.4–2.0 as four major species, $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$, and $[RuCl(H_2O)_5]^{2+}$, whose reduction potentials (peak potentials) are −0.180, −0.270, −0.355, and −0.415 V, corresponding to the couples $[RuCl_4(H_2O)_2]^-/[RuCl_4(H_2O)_2]^{2-}$, $[RuCl_3(H_2O)_3]/[RuCl_3(H_2O)_3]^-$, $[RuCl_2(H_2O)_4]^+/[RuCl_2(H_2O)_4]$, and $[RuCl(H_2O)_5]^{2+}/[RuCl(H_2O)_5]^+$, respectively. All the four reduction steps corresponding to these four couples exist separately at pH 1.0. At pH 0.4 (Figure 2a), however, the potential at −0.255 V may be an average potential of $[RuCl_4(H_2O)_2]^-/[RuCl_4(H_2O)_2]^{2-}$ and $[RuCl_3(H_2O)_3]/[RuCl_3(H_2O)_3]^-$ couples (−0.180 and −0.270 V), which is possible since the former reduction is irreversible and the stability of $[RuCl_4(H_2O)_2]^-$ is greater than that of $[RuCl_3(H_2O)_3]$[8,17] at pH 0.4. The potentials at −0.360 and −0.455 V are thus due to the last two couples.

From Figures 1a′, 2a, and 3a, it is obvious that $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, and $[RuCl(H_2O)_5]^{2+}$ are fairly stable at pH 0.4, moderately stable at pH 1.0, and highly unstable at pH 2.0. The species $[RuCl_2(H_2O)_4]^+$ is, however, fairly stable at pH 2.0. Approximate percentages of these species, with all assumed to be monomeric at the instant of preparation as calculated from their respective peak currents, are presented in Table II.

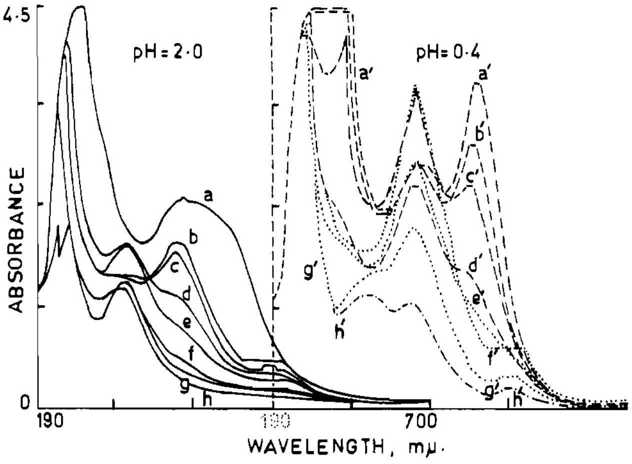

Figure 4. Spectral changes of ruthenium(III) (mM) solution in HCl with time (h) (μ = 0.1 M (KCl), t = 25 °C: (a) 0; (b) 24; (c) 96; (d) 264; (e) 360; (f) 432; (g) 600; (h) 2376; (a′) 0; (b′) 24; (c′) 72; (d′) 96; (e′) 144; (f′) 240; (g′) 480; (h′) 2256.

The steep increase in peak currents for $[RuCl_2(H_2O)_4]^+$ with simultaneous decrease or disappearance in peak heights for $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, and $[RuCl(H_2O)_5]^{2+}$ at pH 0.4 and 1.0 and the presence of a single wave for $[RuCl_2(H_2O)_4]^+$ at pH 2.0 with time undoubtedly show the transformation of stable $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, and $[RuCl(H_2O)_5]^{2+}$ species to a more stable $[RuCl_2(H_2O)_4]^+$ ion. However, when they are allowed to stand, $[RuCl_2(H_2O)_4]^+$ ions tend to attain nonreducibility by polymerization through chloro or hydroxo bridges, which can account for the decrease in peak currents. Perhaps this is the reason for the earlier report[30] of nonreduction of ruthenium at the dropping mercury electrode. Reappearance of small differential pulse peaks around the potentials of $[RuCl_4(H_2O)_2]^-$ and $[RuCl_3(H_2O)_3]$ after a prolonged time show their presence in small concentrations. The appearance of a new polarogram particularly at pH 2.0 after 24 h may be attributed to the hydrolyzed and polymerized species of ruthenium(III) like $[Ru(OH)Cl]_n^{n+}$ and $[ClRu(OH)_2RuCl]^{2+}$.

Coulometry. A millimolar solution of ruthenium(III) chloride instantly after preparation in 0.1 M KCl at pH 2.0, when reduced at a large mercury pool cathode of −0.50 V vs. SCE, accumulates a charge of 0.95 C for reduction of one electron per metal. a similar solution on reduction after storage for 15 days produces a charge of 0.32 C on the electrode surface. The value still gets reduced for solutions stored beyond 15 days, indicating slow polymerization.

Absorption Spectra. The changes in spectral behavior of a millimolar ruthenium(III) chloride solution at pH 0.4 and 2.0 and

Table III. Absorption Spectra for Ruthenium(III) in Hydrochloric Acid at Different Time Intervals

time/24 h[c]	wavelength, nm (ϵ, M^{-1} cm^{-1})[a] pH 0.4	pH 1.0	pH 2.0
0	691 (53), 456 (3644), 377 (2769), 269 (4457), 247 (4446)	691 (45), 456 (3392), 377 (2792), 269 (4480), 247 (4471)	456 (1946), 377 (b) (23), 269 (s) (3039), 245 (4477)
1	685 (60), 449 (2249), 376 (2743), 269 (4511), 250 (4499)	493 (b) (294), 356 (b) (1863), 226 (4110)	496 (b) (560), 371 (1884), 296 (b) (1489), 224 (3982)
3	656 (61), 446 (2491), 376 (3582), 284 (4054), 235 (4177)	661 (86), 557 (123), 494 (b) (348),[b] 367 (1915), 226 (4224)	491 (b) (534), 370 (1825), 296 (b) (1489), 224 (4071)
4	439 (1549), 376 (2524), 274 (s) (2264), 240 (4462)	494 (340), 369 (1845), 300 (s) (1367), 227 (4232)	492 (b) (492), 370 (1757), 300 (b) (1524), 225 (4086)
X	494 (s) (675), 445 (s) (1222), 376 (2747), 283 (s) (1854), 236 (4357)	494 (b) (361), 371 (1894), 300 (s) (1362), 228 (4174)	493 (b) (779), 370 (b) (2605), 307 (2749), 235 (4177)
Y	495 (b) (703), 376 (3738), 238 (4317)	556 (93), 494 (b) (359), 371 (1922), 302 (b) (1322), 230 (4138)	488 (b) (413), 369 (s) (1284), 303 (b) (1843), 228 (4197)
Z	498 (b) (553), 374 (2911), 300 (s) (1686), 236 (4300)	493 (b) (327), 370 () (1600), 311 (b) (1496), 232 (4260)	557 (160), 480 (b) (245), 376 (s) (571), 304 (b) (1418), 219 (3293)
ϕ	497 (b) (374), 373 (2027), 303 (s) (1422), 237 (4297)	556 (53), 488 (b) (129), 365 (b) (653), 308 (b) (787), 217 (3160)	302 (b) (1372), 217 (3203)

[a] Molar extinction coefficients were calculated by using total metal ion concentration; s = shoulder, b = broad. [b] Results obtained on second day. [c] X = 6, 7, and 8, Y = 10, 11, and 11, Z = 16, 18, and 18, and ϕ = 20, 28, and 25 at pH 0.4, 1.0, and 2.0, respectively.

at various time intervals are shown in Figure 4 and the results summarized in Table III. Instantly prepared solutions at pH 0.4 (Figure 4a′) give a weak band at 691 (ϵ 53) nm and intense bands at 456 (3644), 377 (2769), 269 (4457), and 247 (4446) nm. While the band at 691 nm maintained, a new band frequently appears at 556 nm with lowering of intensities. The band at 456 nm undergoes a regular decrease in intensity while that at 377 nm alternatively decreases and increases in intensity with time until it finally diminishes in 100 days. The band at 456 nm, which diminishes in 6 days (Figure 4e′), finally disappears and a new broad band of low intensity appears around 495 nm (Figure 4f′), which disappears slowly after 100 days. The bands at 269 and 247 nm appear to be initially broad for 3 days (Figure 4b′,c′), but after 10 days (Figure 4f′) the former eventually disappears, while the intensity for the latter decreases very slowly with negative shifts. A new band around 300 nm starts to appear beyond 15 days (Figure 4g′) whose intensity decreases in the beginning but stabilizes later when the band at 377 nm disappears.

Similar spectral bands with almost the same molar extinction coefficients (Table III) appear once again for solutions prepared instantly at pH 1.0. The bands at 456 and 377 nm, however, disappear in 1 and 7 days, respectively, and new bands appear around 493 and 300 nm. These new bands disappear after 20 and 100 days, respectively. The intensity of the 247-nm band decreases after 100 days.

At pH 2.0, weak bands were observed at 691 and 557 nm while the bands at 456 and 269 nm appeared as shoulders. The 377-nm band appears as a broad band (Figure 4a) in solution at the instant of preparation. The shoulders at 456 and 269 nm disappear in 30 min, while the 377-nm band diminishes in intensity within 15 days (Figure 4e). Two new bands, one at 491 nm and another at 300 nm, appeared in 1 and 24 h, respectively. The former band disappears after 20 days (Figure 4f), but the intensity of the 300-nm band increases initially for about 15 days (Figure 4b–e) but later decreases and stabilizes between 25 and 100 days (Figure 4f–h).

On comparison of the absorption spectral results (Figure 4a′) with differential pulse polarography results (Figure 2a) of ruthenium(III) chloride solution instantly after preparation at pH 0.4, it is evident that the reduction maximum at −0.455 V and the absorption band at 456 nm were found to disappear at the same time. Similarly, the band around 269 nm and differential pulse peak at −0.255 V diminish uniformly, while the band at 377 nm and the peak currents at −0.360 V steadily change with time. Thus the intense bands at 456, 377, and 269 nm can be assigned to ligand to metal charge transfer (LMCT), $Cl^- \rightarrow Ru(III)$, bands in the species $[RuCl(H_2O)_5]^{2+}$, $[RuCl_2(H_2O)_4]^+$, and $[RuCl_4(H_2O)_2]^-$, respectively. These assignments are well supported by the observations reported by Che et al.[33] wherein a characteristic absorption band at 370 nm was assigned for the ruthenium(III) dichloro complex *trans*-$[Ru(tmc)Cl_2]^+$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) in 0.1 M HCl. Since no band was observed in the region around 269–377 nm, except a minimum at 335 nm whose position and depth depends on time and pH, the characteristic charge-transfer band which is expected to lie between 269 and 377 nm for low-concentration $[RuCl_3(H_2O)_3]$ species might be either closely associated with the band at 377 nm or hidden in the minimum. The irregular band intensity at 377 nm can be attributed to the isomerization of cis or trans species of $[RuCl_2(H_2O)_4]^+$ ions in solution. The high-intensity band at 247 nm, which is affected by extensive polymerization, can be assigned to the outer-sphere ligand to metal charge transfer (OSLMCT) between ionic chloride and cationic ruthenium(III) complexes. Similar types of charge-transfer bands were obtained[34–36] in halide solutions of $[Ru(en)_3]^{3+}$ and $[Ru(NH_3)_6]^{3+}$. The weak bands at 691 (or its shifts), 557, and 494 nm can be assigned to d → d transitions for trivalent ruthenium. Absence of the 494-nm peak in solutions instantly after preparation might be due to its masking by the more intense adjacent band at 456 nm. The absorption maximum around 300 nm and the differential pulse peak at −0.550 V that are observed in solution at pH 2.0 can be assigned to hydrolyzed ruthenium(III) species. The disappearance of spectral bands at 456 and 269 nm assigned as LMCT bands for $[RuCl(H_2O)_5]^+$ and $[RuCl_4(H_2O)_2]^-$ can be accounted for by their instability and transformation to the stable $[RuCl_2(H_2O)_4]^+$ ions. The slow decrease at 377 nm, however, may be attributed to the polymerization of $[RuCl_2(H_2O)_4]^+$ ions.

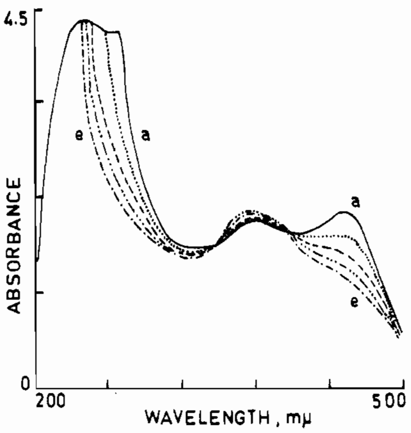

Figure 5. High-speed time-drive absorption of ruthenium(III) chloro complexes in HCl at different times (min) ([Ru(III)] = 0.75 mM, pH 2.0, [KCl] = 0.1 M): (a) 0; (b) 10; (c) 20; (d) 30; (e) 40.

Though Connick et al.[16,17] succeeded in isolating individual chloro complexes by elution methods, they failed to get reproducible spectrophotometric results. There were always discrepancies in their molar extinction coefficients and those of others,[18] for which proper explanation could not be given. The uncertainty and time-dependent spectral behavior of ruthenium(III) in chloride medium as found in these investigations was the main cause for these discrepancies.

High-Speed Time-Drive Absorption Spectra. The conversion of chloro species in solution (pH 0.4, 1.0, and 2.0) are substantiated by the formation of two isosbestic points at 346 and 405 nm in high-speed time-drive absorption spectra as demonstrated in Figure 5. These isosbestic points arise due to the regular decay of the bands at 456 nm ($[RuCl(H_2O)_5]^{2+}$) and 269 nm ($[RuCl_4(H_2O)_2]^-$ with simultaneous increase in the intensity of the band at 377 nm ($[RuCl_2(H_2O)_4]^+$). The band at 456 nm does not hold its isosbesticity after 30 min due to the polymerization of $[RuCl(H_2O)_5]^{2+}$ ions at pH 0.4 and 1.0 along with hydrolysis at pH 2.0. Preliminary data on the decay of these charge-transfer bands show that the conversion rates are inversely proportional to the metal ion and hydrogen ion concentrations.

Temperature Effect. When instantly prepared ruthenium(III) solutions at pH 1.0 are heated to 70 °C for 10 min the peak heights at −0.355 V in differential pulse polarography and 377 nm in absorption spectra for $[RuCl_2(H_2O)_4]^+$ ions gain in intensity, while the rest of the peaks decrease. The changes are pronounced in solutions heated to boil, indicating the fast equilibrium between chloro complexes at higher temperatures.

Conclusions

The distribution of ruthenium(III) species with pH, based on the results of electrochemical and absorption spectroscopy analysis, is presented in Figure 6. It is clear from Figure 6 that the most stable species of ruthenium(III) chloride present instantly after preparation of the solution in highly acidic solution (pH <0.4) is $[RuCl_4(H_2O)_2]^-$. The species is stabilized by increasing hydrogen ion concentration probably due to hydrogen bonding to form ions like $[RuCl_4(H_2O)_2]^- \cdots [\cdots H^+ \cdots [RuCl_4(H_2O)_2]^- \cdots]_n \cdots H^+$, where *n* is an integer. According to the findings of Fine[37] and

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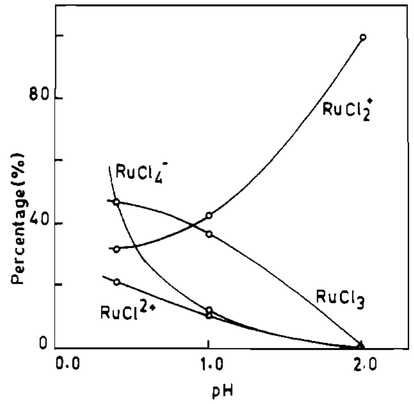
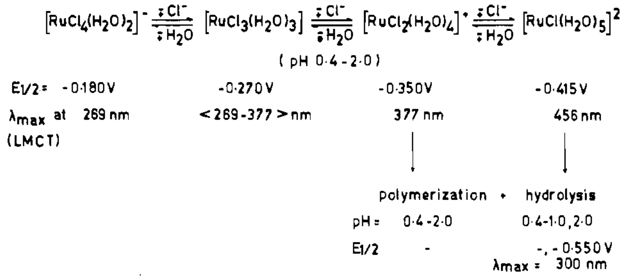


Figure 6. Distribution of the percentage of ruthenium(III) chloro complexes with solution pH (t = 25 °C, μ = 0.1 M (KCl)).

Scheme I



Halpern et al.,[8] these species are highly labile and exist to a maximum concentration in hydrochloric acid upto 4 N. These labile species on dilution to lower pH (0.4–2.0) dissociate to their lower chloro complexes and attain an equilibrium in solution as described in Scheme I. Of these species, $[RuCl_2(H_2O)_4]^+$ ions are the most stable in the pH range investigated and the rest, which are less stable, get converted to the former stable species under the experimental conditions. However, when they age, $[RuCl_2(H_2O)_4]^+$ ions become unstable and polymerize extensively as evidenced by nonreducibility at the DME. The species $[RuCl(H_2O)_5]^{2+}$ also undergo polymerization (pH 0.4 and 1.0) along with hydrolysis (pH 2.0).

Moreover, the observation of the color changes in experimental solutions from yellowish brown to light yellow (pH 0.4), colorless (pH 1.0), and light brick red (pH 2.0), slow precipitation in stored solutions at pH 7.0, and immediate formation of black precipitate at pH 3.0 strengthen the formation of polymeric species in solution.

The equilibria existing in solutions for the various ruthenium(III)–chloro species in the pH range studied may be expressed by

$$[RuCl(H_2O)_5]^{2+} + Cl^- \overset{K_1}{\rightleftharpoons} [RuCl_2(H_2O)_4]^+ + H_2O \quad (1)$$

$$[RuCl_2(H_2O)_4]^+ + Cl^- \overset{K_2}{\rightleftharpoons} [RuCl_3(H_2O)_3] + H_2O \quad (2)$$

$$[RuCl_3(H_2O)_3] + Cl^- \overset{K_3}{\rightleftharpoons} [RuCl_4(H_2O)_2]^- + H_2O \quad (3)$$

With use of the data on the percentage of each species (Figure 6) in solution, these constants K_1, K_2, and K_3 ($0.4 < pH < 2.0$) can be calculated with the help of appropriate equations by assuming a constant excess of chloride ion concentration. These constants at 25 °C (μ = 0.1 M KCl, pH 1.0) are 4.05, 0.86, and 0.33, respectively.

The constants K_1, K_2, and K_3 reported by Ohyoshi et al.[19] in $HClO_4$–HCl medium at 6 °C (μ = 0.46) with the help of the electrophoresis technique are 20, 2.8, and 0.6, respectively. These values, however, cannot be compared directly with our results because of the difference in experimental conditions.

Registry No. $[RuCl(H_2O)_5]^{2+}$, 26167-23-7; $[RuCl(H_2O)_5]^+$, 35594-90-2; $[RuCl_2(H_2O)_4]^+$, 99922-04-0; $[RuCl_2(H_2O)_4]$, 100017-79-6; $[RuCl_3(H_2O)_3]$, 15203-91-5; $[RuCl_3(H_2O)_3]^-$, 99922-05-1; $[RuCl_4(H_2O)_2]^-$, 100017-77-4; $[RuCl_4(H_2O)_2]^{2-}$, 100017-78-5; Ru, 7440-18-8; KCl, 7447-40-7.

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Formation of Actinide Hexafluorides at Ambient Temperatures with Krypton Difluoride

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A second low-temperature agent, krypton difluoride, for generating volatile plutonium hexafluoride is reported (dioxygen difluoride is the only other reported agent). Plutonium hexafluoride is formed at ambient or lower temperature by the treatment of various solid substrates with krypton difluoride. Volatilization of uranium and neptunium from solid substrates using *gaseous* krypton difluoride is also reported for the first time. The formation of actinide hexafluorides has been confirmed for the reaction of krypton difluoride in anhydrous HF with UO_2 and with uranium and neptunium fluorides at ambient temperatures. Treatment of americium dioxide with krypton difluoride did not yield americium hexafluoride under the conditions studied.

Introduction

The use of elemental fluorine on uranium, neptunium, and plutonium substrates at or above 300 °C has been the only known method of economically converting these materials to the volatile hexafluorides.[1-3] We recently reported that ambient-temperature dioxygen difluoride (O_2F_2) gas will smoothly and efficiently convert U_3O_8 to UF_6.[4] Plutonium tetrafluoride, oxide, and oxyfluorides are all readily fluorinated to PuF_6 by gaseous O_2F_2 or O_2F_2/HF solutions at *or below* room temperature.[5] Similarly, we have shown that neptunium substrates can be fluorinated to NpF_6 with dioxygen difluoride.[6]

Soviet authors Drobyshevskii et al.[7,8] have reported the ambient-temperature or lower temperature fluorination of the oxides and tetrafluorides of uranium, neptunium, and americium and the oxyfluorides of neptunium with krypton difluoride in bromine

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