THE BEHAVIOUR OF RUTHENIUM TRICHLORIDE IN AQUEOUS SOLUTIONS

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SUMMARY

Alkalimetric and argentometric titrations on the so-called "ruthenium trichloride" show the formation of hydroxycomplexes in aqueous solutions and mixtures of chlorohydroxy- and chloro-complexes in the presence of alkali chloride and HCl. Two absorption maxima are observed in the spectrum in the ranges of 390 and 460 m μ . The reduction to Ru(II) and a further reduction can be recorded polarographically, as well as the catalytic discharge of H⁺. The results are in agreement with the presence of ruthenium in the +4 valency state.

INTRODUCTION

The commercially available so-called "ruthenium trichloride" has been said in earlier papers to contain trivalent ruthenium¹ but some evidence has recently been given for the presence of the +4 oxidation state². It was thought that an investigation of the behaviour of this compound in aqueous solution might throw further light on this argument.

As a matter of fact, the available literature generally concerns ruthenium compounds other than ruthenium trichloride. The redox potentials in a non-complexing medium have been studied^{3,4} as well as the polarography of Ru(IV) in perchloric solutions⁵. By using ion-exchange resins for chloride solutions, some indications of Ru(IV) – chlorocomplexes were obtained⁶ and evidence was given for the species RuCl₂⁺ in the +3 oxidation state⁷. A compound intermediate between Ru³⁺ and Ru⁴⁺ was obtained by PSHENITSYN AND GINSBURG⁸ by spectrophotometric titration of K₂RuOHCl₅ with TiCl₃. A great deal of information on the spectrophotometry of Ru(IV)-chlorocomplexes has been given by WEHNER AND HINDMAN⁹, whose results will be taken into account later in this paper. More recently PSHENITSYN AND EZERSKAYA¹⁰ have investigated the behaviour of K₂RuCl₅OH and K₂RuCl₅·H₂O at the platinum electrode.

EXPERIMENTAL

Solutions were prepared from hydrated ruthenium trichloride, purchased from Th. Schuchardt, Munchen. Analysis of this compound gave 43.7% Ru and 46.1% Cl, corresponding nearly to a 1:3 molar ratio.

Apparatus

This consisted of a Metrohm E 148 C potentiometer-pH meter, with a glass

electrode, a silver electrode and a saturated calomel reference electrode; a Beckman DU spectrophotometer, with I-cm corex glass cells; a Leybold polarograph with photographic recording. Spectra and polarograms were recorded on stabilized solutions in each case after 3-6 days.

RESULTS AND DISCUSSION

Potentiometric titrations

A freshly prepared aqueous solution of hydrated ruthenium trichloride has a deep red colour, which becomes darker in a few minutes, owing to hydrolysis. Several days are necessary in order to reach stabilization at room temperature of such a

TABLE I Argentometric titration of Cl⁻ on solutions of ruthenium trichloride in various SUPPORTING ELECTROLYTES

Supporting electrolyte	Percent Cl=* found after:			
	30 min	1 day	3 days	1 week
H ₂ O	88	93	97	~ 100
0.1 <i>M</i> NaCl	79	79	82	∼ 90
0.1 M HClO ₄	82	88	94	- 96
t M HClO ₄	~ 80	~ 80	~ 80	∼ 80
0.01 M HCl	84	92	95	97
0.05 M HCl	72	80	86	89
0.1 M HCl	62	70	75	\sim 80
$0.1 M HCl + 1 M HClO_4$	64	63	65	66

* When Cl⁻ was present in the supporting electrolyte, a correction was made for the blank. The value 100% means three Cl- per mole of ruthenium.



Fig. 1. Alkalimetric titrations of 8 mM ruthenium trichloride in 25 ml of: A, o M; B, o.5 M; C, 1.5 M; D, 4.8 M NaCl.

solution; by heating at 100°C a shorter time is required but the results are characterized by a lower reproducibility. In the presence of NaCl less hydrolysis is observed, the colour of the solutions tending more toward a red tone at higher NaCl concentrations. In order to obtain a measure of this hydrolysis, potentiometric measurements of pH were carried out by comparison with HCl at the same ionic strength; they showed the pres-

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ence of 2.0, 1.6, 0.8 and 0.4 free H⁺ ions per mole of Ru respectively in 0, 0.5, 1.5 and 5 M NaCl. On the other hand an argentometric titration on a stabilized aqueous solution yielded 3 Cl⁻ per mole of Ru, while in the presence of NaCl a lower amount of free chloride ions was found (Table I). When no NaCl is added, no stable ruthenium—chloro-complexes but only some hydroxycomplexes are present; in the presence of NaCl some chloro—hydroxycomplexes are formed with a decrease in the amount of coordinated OH⁻, at higher Cl⁻ concentrations. In agreement with this hypothesis, the alkalimetric titrations show two steps when the pH is plotted against the volume of alkali, as in Fig. 1: the second is due to the complete precipitation of ruthenium hydroxide; the first, which is more evident in highly concentrated NaCl, must be attributed to the titration of free H⁺ ions, whose presence is due to hydrolysis.



Fig. 2. Argentometric titrations of 10 mg hydrated ruthenium trichloride in 25 ml of: A, o M; B, O.I M; C, I M; D, 2 M HClO₄.

In the presence of a non-complexing acid such as $HClO_4$, less than 3 Cl⁻ per mole of Ru is found by titration: some data are given in Table I and the titration curves in Fig. 2. A stepwise variation of the potential can be observed as $[H^+]$ increases up to 2 M, giving evidence for the presence of a mixture of chlorocomplexes, whose formation is favoured since hydroxycomplexes are present in smaller amounts in acid solution. By working in HCl solutions, the formation of chlorocomplexes becomes evident owing to the simultaneous action of both H⁺ and Cl⁻: as indicated by the data in Table I, a relatively low concentration of HCl is sufficient to produce an amount of free chloride ions substantially less than 3 Cl⁻ per mole of Ru. In general, alkalimetric and argentometric titrations, although not able to establish individually the valency state of ruthenium, may however show the presence of complex hydrolysis equilibria.

Spectrophotometric characteristics

The darkish aqueous solutions of ruthenium trichloride do not give a well defined absorption spectrum, owing to the colloidal character of the highly hydrolyzed species. On the other hand, in the presence of a high concentration of chloride ions,

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an absorption maximum appears at 425 m μ (Fig. 3A), with a molar extinction coefficient $\varepsilon_{max} = 4100$. By a small increase of the acidity, two new maxima are produced in the ranges of 390 and 460 m μ (Fig. 3B); this fact could be attributed to the transformation from highly basic complexes to ones containing a lower amount of coordinated OH⁻. At a high concentration of Cl⁻, a slight acidity is able to produce



Fig. 3. Spectra of 1 mg ruthenium trichloride in 25 ml of 3 M (NaCl + HCl); the H⁺ concentration is: A, o M (hydrolysis only); B, 0.003 M; C, 0.01 M; D, 3 M.



Fig. 4. Spectra of I mg ruthenium trichloride in 25 ml of: A, o.I M HCl; B, o.I M HCl + I M HClO₄; C, o.I M HCl + 8 M HClO₄.

this change: a further increase of $[H^+]$ causes only a slight variation in the spectrum (Fig. 3C and D). At low concentrations of Cl⁻, a large variation in the acidity is necessary in order to observe a significant change in the spectrum, as can be observed from Fig. 4.

The spectra obtained in solutions containing 1-10 M HCl are shown in Fig. 5. The

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first maximum increases markedly, while the second undergoes a decrease and a shift towards higher wavelengths. The following values of molar extinction coefficients were found: in 1 *M* HCl, ε_{\max} is 3000 at 385 m μ and 4200 at 465 m μ . In 10 *M* HCl: 6200 at 375 m μ and 2900 at 480 m μ . In 0.6 *M* HCl the first maximum nearly disappears and the second attains the highest value of ε_{\max} ; at lower concentrations of HCl the second maximum also decreases.



Fig. 5. Spectra of 1 mg ruthenium trichloride in 25 ml of: A, 1 M; B, 2 M; C, 3 M; D, 5 M; E, 10 M HCl.

TABLE II

Data by Wehner and Hindman		Conditions for the same spectral characteristics	
Complex form	$\lambda_{max}(m\mu)$	Emax	by using Ru trichloride
Ru(OH) ₂ Cl ⁺ (?)	~ 420		3 M NaCl
Ru(OH) ₂ Cl ₂ (H ₂ O) ₂	562	16400	Unstable form, present only for a short
	427	5000	time in any solution
$Ru(OH)_2Cl_3(H_2O)^-$	454	6100	∼ 0.6 M HCl
Ru(OH) ₂ Cl ₄ ² -	385	8140	8–10 M HCl
. ,	476	4500	
Ru(OH)Cl ₅ ²⁻ (?)	~ 360		>10 M HCl, or by using $(NH_4)_2RuCl_6$

These spectrophotometric results are in a fair agreement with those given by WEHNER AND HINDMAN⁹ and obtained from solutions of Ru⁴⁺. In Table II are reported the characteristics of several chlorocomplexes, characterized by these authors, and the conditions under which similar data were obtained in the present work, starting from ruthenium trichloride. Small differences were found in the values of ε_{\max} , but one must take into account that the data by WEHNER AND HINDMAN

refer to the single complexes, while in our solutions mixtures of complexes are always present and ε_{\max} is calculated on the basis of the total ruthenium.

The spectrum in 3 M NaCl is similar to the one attributed to Ru(OH)₂Cl+; however, owing to the large influence of $[H^+]$ on the spectrum (Fig. 3), it may be justifiable to ascribe a different amount of coordinated OH⁻ to this species, with respect to the higher chlorocomplexes.

The presence of the bichlorocomplex, with λ_{max} at 565 m μ , was demonstrated only for a few minutes after ruthenium trichloride was dissolved; no indication of this species was observed in stabilized solutions.

The change in the spectra reported in Fig. 5 may be ascribed to a mixture of triand tetra-chlorocomplexes. The shift of λ_{max} towards ~ 360 m μ for high [HCl] was tentatively attributed by WEHNER AND HINDMAN to the pentachlorocomplex. An unstable spectrum with $\lambda_{max} = 360 \text{ m}\mu$, however, was recorded in the present work using freshly prepared solutions of (NH₄)₂RuCl₆, therefore this maximum is more probably due to the presence of the hexachlorocomplex.

It is evident however from these comparisons that "ruthenium trichloride" contains ruthenium in the +4 valency state.

Polarographic behaviour

When the reduction of ruthenium trichloride at the dropping mercury electrode is recorded, a wave is obtained which shows two steps of almost the same height; the



Fig. 6. Polarogram of 1.6 mM ruthenium trichloride in 0.1 M HCl + 2 M NaCl with 0.01% gelatin: -0.2, -0.3, -0.4 and -0.5 V/S.C.E. are indicated.

first begins immediately after the anodic wave of Cl-, the current becoming cathodic at the more negative applied voltage the higher the [Cl-]. The second is sufficiently well defined (see Fig. 6) and therefore its characteristics can be investigated. Both steps are proportional to the ruthenium concentration over the range 0.1-5 mM; for lower values however the steps are not so clearly divided. Half-wave potentials (the values of E_{t} are in any case those of the second step) are shifted in accord with the

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ruthenium concentration: the following values were observed in 0.4 M KCl + 0.1 M HCl: -0.300, -0.318, -0.342, -0.359 and -0.368 V/S.C.E., respectively for 1, 2, 3, 4 and 5 mM Ru at 25°C.

Both the steps are proportional to the square root of the mercury column height. When the temperature is increased (Table III) the second step shows a higher slope and is shifted to less negative potentials about $1 \text{ mV}/^{\circ}\text{C}$; these facts give some evidence for the irreversibility of the reduction. As a maximum is sometimes apparent at the beginning of the diffusion current in the second step, 0.01% gelatin can be added to suppress it; in any case such a substance causes the step to be shifted to more negative potentials.

t(°C)	First step ia(µA)	ia(µA)	Second step E _{3/4} – E _{1/4} (mV)	$E_{1/2} \ (V/S.C.E.)$	
17	6.74	7.92	97	-0.345	
25	7.37	8.83	100	—0.336	
35	8.45	10.73	110	-0.325	
45	9.44	13.48	115	-0.312	
55	10.40	15.8	116	0.303	
65	11.08	18,6	120	0.298	
verage variation per degree	+ I . I %	+ 1.9%		+τ mV	

TABLE II]	
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variation of polarographic characteristics with temperature: 3 mM ruthenium trichloride in 0.3 M KCl + 0.1 M HCl



Fig. 7. Polarogram of 1 mM bivalent ruthenium (blue form, after reduction with Zn) in 2 M HCl + 2 M NaCl: --0.2, --0.3, --0.4 and ---0.5 V/S.C.E. are indicated.

In 1-5 M NaCl well defined polarograms can be obtained, the acidity being only that due to the hydrolysis; on the contrary, when the supporting electrolyte is less concentrated than 1 M, the darkish solutions containing basic complexes are not able to yield well developed curves. In HCl solutions a variation of E_{1} is observed, in agreement with the presence of chlorocomplexes; the values -0.354, -0.377, -0.396,

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-0.411 and -0.424 V/S.C.E. were found at 25°C respectively in 1, 2, 3, 4 and 5 M HCl, $\lceil Ru \rceil$ being 1.5 mM.

After reduction of ruthenium by Zn to the well known blue Ru(II), a step such as is shown in Fig. 7 can be recorded in the same range as the second step of ruthenium trichloride. Since the starting material is Ru⁴⁺, as shown by the spectrophotometric results, the first step in the above-mentioned polarograms could correspond to the reduction from Ru(IV) to Ru(II), which should then undergo a further reduction to metal in the second step.



Fig. 8. Polarograms of 1 mM Ru HCl + 0.01 mM in 0.2 M KCl: $h_{Hg} = 42.0$ mm (A) and 24.7 mm (B); -1.35 and -1.5 V/S.C.E. are indicated for each curve.

Finally, the catalytic discharge of H⁺ can be clearly observed under such conditions as are shown in Fig. 8; the wave appears to be divided into two parts: the first corresponds to the reduction of H⁺, catalyzed by the presence of ruthenium in the ratio 1:100; the second is the usual hydrogen wave. The curves are recorded at different mercury column heights: it is easy to note that the catalytic step is not affected by such a variation, while the usual step increases more than proportionally with $l/h_{\rm Hg}$, so that the whole H⁺ current undergoes a regular variation.

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