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EFFECT OF HYDROGEN-ION CONCENTRATION ON THE POLAROGRAPHIC REDUCTION OF PENTAAMMINERUTHENIUM(III) COMPLEX

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Polarographic studies have been made on a series of pentaammineruthenium(III) complexes in various acidic solutions. The reduction process was found to be a reversible one with an electron-transfer at the dropping mercury electrode. The effect of hydrogen-ion concentration was markedly observed on the half-wave potential, i.e., its value shifted to the positive side with the increase in the hydrogen-ion concentration. This can be interpreted by assuming that the protonation occurs prior to the electrode process, so the electron density of ruthenium ion decreases.

There have been reported some polarographic researches on the cobalt(III) and platinum(IV) complexes, but similar studies on the ruthenium(III) complex are rather scarce. The recent polarography of ruthenium(III) complex[1,2] represented that they are reversibly reduced through one electron-transfer process. The present paper deals with the polarography of several carboxylatopentaammineruthenium(III) complexes to investigate the effect of hydrogen-ion concentration on the polarographic stability and to compare with the results of their hydrolysis reactions.[3]

All the chemicals used were of a reagent grade. Twice-distilled water was used in all the experiments. The ionic strength and the acidity of the electrolyte were adjusted with p-toluenesulfonic acid and its sodium salt.

Formatopentaammineruthenium(III) and other carboxylatopentaammineruthenium(III) complexes were prepared by the method of Stritar and Taube[4] from chloropentaammineruthenium(III) chloride, a carboxylate buffer solution, and zinc amalgam. Found: C, 2.95; H, 3.65; N, 16.36%. Calcd for $[RuO_2CH(NH_3)_5](ClO_4)_2$: C, 2.79; H, 3.75; N, 16.28%. Found: C, 5.35; H, 3.96; N, 15.66%. Calcd for $[RuO_2CCH_3(NH_3)_5](ClO_4)_2$: C, 5.41; H, 4.08; N, 15.77%. Found: C, 7.90; H, 4.31; N, 15.25%. Calcd for $[RuO_2CC_2H_5](ClO_4)_2$: C, 7.86; H, 4.41; N, 15.28%. Found: C, 10.42; H, 4.42; N, 14.73%. Calcd for $[RuO_2CC_3H_7](ClO_4)_2$: C, 10.17; H, 4.70; N, 14.83%. Found: C, 5.38; H, 3.85; N, 15.07%. Calcd for $[RuO_2CCH_2\text{-}OH(NH_3)_5](ClO_4)_2$: C, 5.22; H, 3.94; N, 15.22%. Found: C, 4.37; H, 3.70; N, 14.85%. Calcd for $[RuO_2CCH_3NH_3(NH_3)_5](ClO_4)_3$: C, 4.28; H, 3.60; N, 14.99%.

A Shimazu RP-50 polarograph was employed with the circuit for extendable and adjustable e.m.f. An H-cell with a saturated calomel electrode was used. The capillary used had an m-value of 1.82 mg/sec and a drop time of 5.0 sec/drop in distilled water at the mercury height of 61.5 cm with an open circuit. All measurements were carried out in a thermostat of 25.0 ± 0.1°C. A gelatin solution(0.01%) was used as a maximum suppressor. Oxygen was removed from the solution of p-toluenesulfonic acid and its sodium salt(0.2M) by bubbling nitrogen gas through it for about 30 min, preventing the evaporation. Polarographic measurements were made as soon as possible after the removal of oxygen. The half-wave potentials were determined from the enlarged polarograms by plotting method. The potential values were calibrated for IR drop, using the minimum value of the cell resistance.

All the complex ions gave rise to well-defined polarographic reduction waves of one step. For each complex, graphical plots of diffusion current, i_d, vs. concentration are linear, and pass through the origin. Plots of i_d vs. the square root of the mercury column height, h, are linear. The electrode process therefore possesses a high degree of diffusion control. Plots of $E_{d.e.}$ vs. log $i/(i_d - i)$ are almost linear for all complexes. In each case the slope of this plot is 60 ± 2 mV, indicating that the electrode reaction is a reversible one-electron step. The half-wave potentials of the complexes are given in Table 1. All the complexes were reversibly reduced in a step at the D.M.E., but considerable differences in the values of $E_{1/2}$ were observed at two different pH values of electrolyte.

Table 1. Half-wave potentials in acidic and neutral electrolyte of $[Ru(NH_3)_5X]^{2+}$.

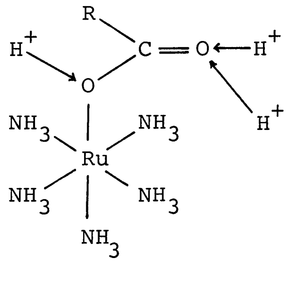
X	$-E_{1/2}$ V vs.	S.C.E.	difference	$\Delta H^{\ddagger}$, kcal·mol^{-1} a)		difference	pKa for ligand acid b)
	pH, 2.10	pH, 7.00		for k_H	for k_{H_2O}		
Formato-	0.268	0.282	0.014	17.48	20.18	2.70	3.75
Acetato-	0.253	0.330	0.077	18.94	24.14	5.20	4.76
Propionato-	0.263	0.338	0.075	18.05	29.64	11.58	4.87
Butyrato-	0.270	0.343	0.073	19.02	24.70	5.68	4.86
Glycolato-	0.290	0.311	0.021	21.56	23.33	1.77	3.83
Glycino-	0.294	0.288	-0.006	32.62	24.34	-8.28	pK_1 2.35 pK_2 9.78

a) These values were obtained from the rate constants in ref. (3) by the further simulation analysis.

b) Ref. (5)

As is shown in Table 1, the half-wave potential values obtained in acidic solutions are generally more positive than those in neutral solutions. This trend is in agreement with that of the activation enthalpies for the aquation and acid hydrolysis reactions. The similarity observed in the relative reactivities for the two kinds of the reactions may be related with the electronic population affecting both the electron transfer and the aquation reactions. In particular, the contribution of the hydronium ion on both reactions suggests the decrease of electronic population on the ruthenium (III) ion in the protonated complex species.

Some remarks should be here made of the molecular interaction between carboxylatopentaammineruthenium(III) complexes ($(NH_3)_5RuOC(=O)R^{2+}$) and acid catalyst H^+; Three distinctive modes of the interaction can be allowed in view of orbital symmetry and orbital energies of both species as bellow:



Ru-O=2.5Å; Ru-N=2.23Å; N-H=1.031Å; C-O=1.28 - 1.43Å

∠RuOC=105°; ∠OCO=122.4 - 130°

The preliminary calculations of all-valence-shell-electron extended Hückel MO on the above interacting system of $(NH_3)_5$-

$RuOC(=O)R^{2+}—H^{+}$ 6) have demonstrated that the most plausible interaction of the H^{+} catalyst occurs predominantly in the direction of the orbital expansion of nonbonding lone-pair 2p-orbital on the oxygen atom of Ru-O bond in terms of the weakening of the Ru-O: in the case of $(NH_3)_5RuOC(=O)H^{2+}$, the bond population of Ru-O (0.085) was lessened to be 0.073 by the electrophilic attack of the H^{+} catalyst (H^{+}—O ≥0.97 Å). It is worthy of emphasis that the single C-O bond is not weakened by the attack of the catalyst and that, in some measure, the solvent of H_2O participates in the weakening of the Ru-O bond.

The pH dependence of $E_{1/2}$ has been measured for the propionatocomplex. As is shown in Fig. 1, the remarkable dependence is found in the pH region from 2 to 4, while it is a little in the region of pH>5. The similar relationship has been observed in the case of the polarographic reduction of the fluoropentaamminecobalt(III) complex 7). The analysis of this pH dependence of $E_{1/2}$ indicates that the complex is protonated and then reduced with a greater rate constant of the electrode reaction proper. Thus, the reaction scheme can be represented as follows.

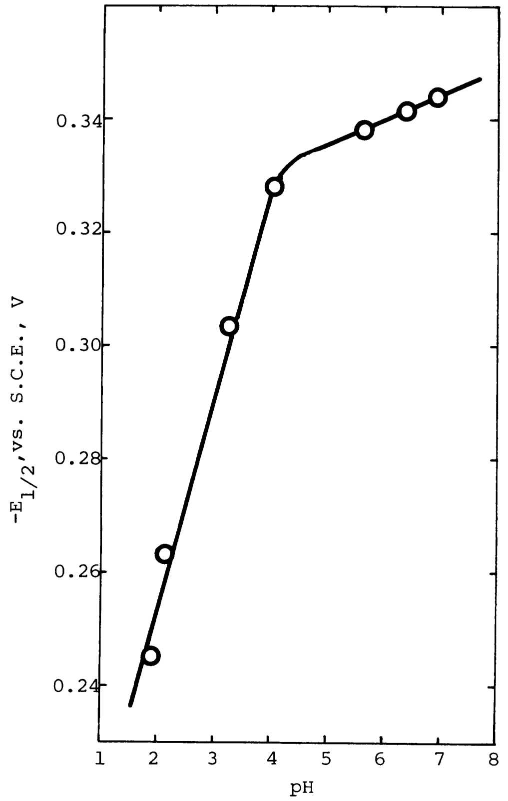


Fig.1. Plot of $E_{1/2}$ vs. pH
complex: propionatopentaammine-ruthenium(III)
temp: 25.0°C, t_1: 5.0 sec
electrolyte: 0.1 M p-toluenesulfonic-sulfonate solution

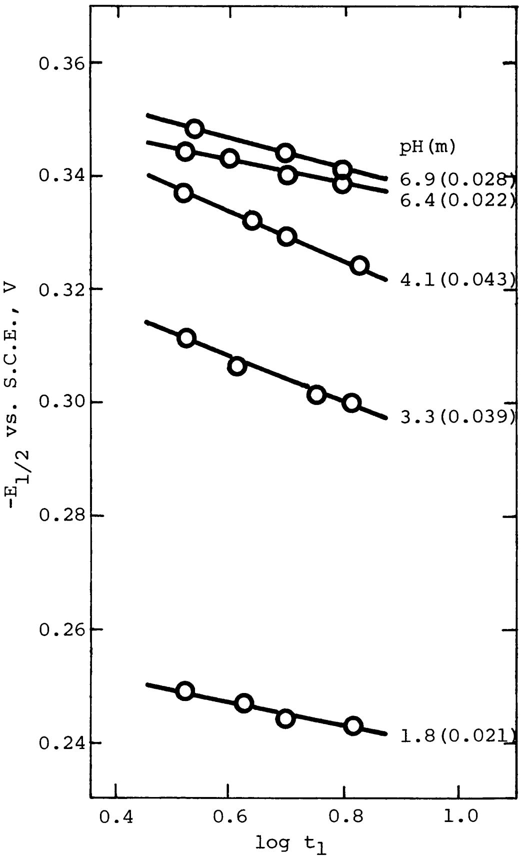
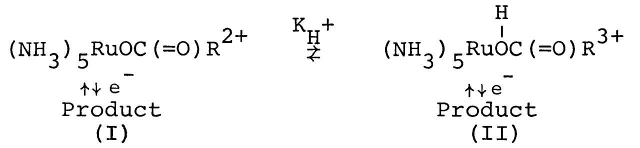


Fig.2. Plots of $E_{1/2}$ vs. log t_1
complex: propionatopentaammine-ruthenium(III)
temp: 25.0°C



$$\underset{\underset{\text{(I)}}{\text{Product}}}{\underset{\uparrow\downarrow e^-}{(NH_3)_5RuOC(=O)R^{2+}}} \quad \overset{K_{H^+}}{\rightleftarrows} \quad \underset{\underset{\text{(II)}}{\text{Product}}}{\underset{\uparrow\downarrow e^-}{(NH_3)_5Ru\overset{H}{O}C(=O)R^{3+}}}$$

The electrode reaction proper proceeds via two parallel paths and the rate constant of reaction(I) is somewhat less than that of the reaction(II). These reaction scheme are fairly in agreement with those having the two different reaction paths, i.e., the acid-catalysed path and the acid-uncatalysed one in the aquation reaction.[3)]

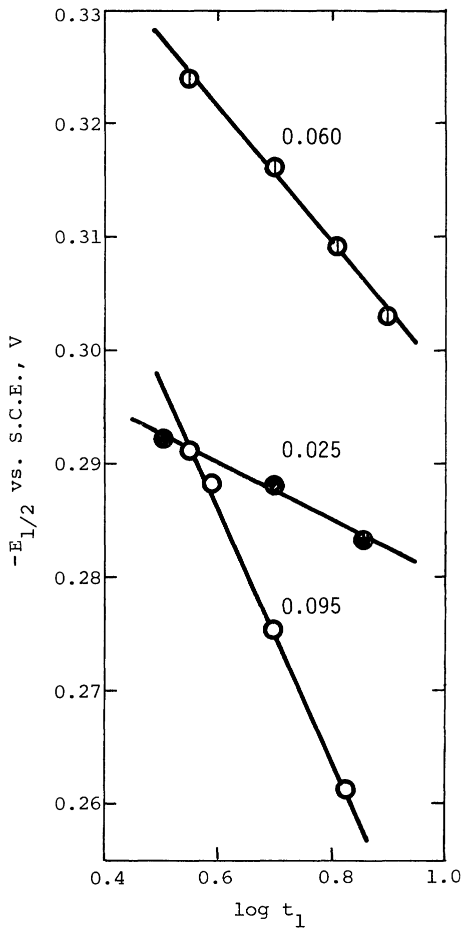
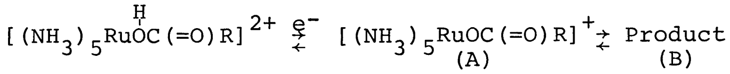


Fig.3. Plots of $E_{1/2}$ vs. log t_1

o: formatocomplex
◐: glycolatocomplex
●: glycinatocomplex

temp: 25.0°C, pH: 7.0

The measurements of $E_{1/2}$ were made at different mercury drop times (t_1) in various acidic solutions of propionatocomplex and in solutions containing various complexes at a constant pH. The results are presented graphically in Figs.2 and 3. Positive shifts of $E_{1/2}$ with increasing t_1 were observed for the propionatocomplex in all the pH of experiments, but the lines show different gradients which increase with the increase in the pH of solution. As is shown in Fig.3, the gradient of a similar plot for each complex is also different. Since it has been established that the electrode process of all the complexes is considerably reversible one, this positive shift of half-wave potential suggests an existence of subsequent reaction after the reversible electrode process.



$$[(NH_3)_5Ru\overset{H}{O}C(=O)R]^{2+} \overset{e^-}{\rightleftarrows} \underset{(A)}{[(NH_3)_5RuOC(=O)R]^{+}} \rightleftarrows \underset{(B)}{\text{Product}}$$

For the relationship between $E_{1/2}$ and log t_1, the simplified equation has been given by the expression[7)]; $E_{1/2} = E^0 + RT/nF\ln 0.086\sqrt{\rho\sigma t_1}$, where ρ represents the formal rate constant of the formation of the electroactive species A and σ is the ratio of the equilibrium concentrations of inactive(B) to active form(A). This simplification has been made on the basis of the assumption that the equilibrium is shifted almost completely towards B. The equation is reformed as follows: $E_{1/2}$ = const. + 0.029 log t_1. As is shown in Figs.2 and 3, the plots of $E_{1/2}$ vs. log t_1 give straight lines with different gradients. This may suggest that the more complex subsequent reaction occurs and gives some irreversibilities to the electrode process.

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