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The Polarographic Reduction and UV Spectral Properties of Pentaamminecarboxylatoruthenium(III) Complexes

Akira Ohyoshi* and Kenichiro Yoshikuni
Department of Industrial Chemistry, Kumamoto University, Kumamoto 860

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Synopsis. Pentaamminecarboxylatoruthenium(III) complexes are reversibly reduced to the corresponding Ru(II) complexes by means of a one-electron transfer at the dropping mercury electrode in aqueous solutions. The absorption maxima, which ranged from 34.6×10^3 cm^{-1} (trichloroacetato complex) to 33.6×10^3 cm^{-1} (glycinato complex) were assigned to the charge-transfer from ligand to metal; they were linearly related to the reversible half-wave potential.

Recent polarographic reduction studies of ruthenium(III) carboxylato complexes[1–3] have revealed that the complexes are reversibly reduced at the dropping mercury electrode through the process of one-electron-transfer. For the series of ammineruthenium(II, III) complexes,[4–9] formal reduction potentials (E_f) were measured and a linear relationship was found to exist between the E_f and the charge-transfer energy from metal to ligand.[8] Hence, it seemed of interest to check whether or not a similar relationship exists between the $E_{1/2}$ and the CT-energy from ligand to metal for ruthenium(III) complexes. In the present paper, a similar relationship was confirmed between them for the series of Ru(III) complexes.

Experimental

Reagents and Materials. 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 solution were adjusted with *p*-toluenesulfonic acid and its sodium salt. Pentaammineformatoruthenium(III) and other carboxylato complexes were prepared by the method described in the literature[10] starting from pentaamminechlororuthenium(III) chloride, the corresponding buffer solution, and zinc amalgam. The complexes thus prepared were analyzed by the usual elemental analysis, and their chemical purities were confirmed.

Apparatus and Procedures. A Shimadzu RP-50 polarograph was employed with a circuit for an extendable and adjustable applied potential. An H-cell with a saturated calomel electrode (SCE) was used. The capillary used had an *m*-value of 1.82 mg s^{-1} and a drop time of 5.0 s in distilled water at a mercury height of 61.5 cm with an open circuit. All the measurements were carried out in a thermostat of (25.0±0.1) °C. Gelatin was used as the maximum suppressor. Polarographic measurements were made after the removal of oxygen by bubbling nitrogen gas through the electrolyte solution. The half-wave potentials were determined from the extended polarograms by means of the plotting. The potential values were corrected for the *iR* drop by using the minimum value of the cell resistance. A Shimadzu UV-200 spectrophotometer was used to measure the electronic spectra of the ruthenium complexes.

Results and Discussion

Electrode Process in the Polarographic Reduction of a Complex. Each complex exhibits a single well-defined reduction wave at a potential near zero volt *vs.* SCE. The limiting current, i_l, was proportional to the concentration of the complex ion. Plots of i_l *vs.* the square root of the mercury head, h, were linear. Thus, the electrode process posseses a high degree of diffusion control. The plots of $E_{d.e.}$ *vs.* $\log[i/(i_d-i)]$ are almost linear for all the complexes (Fig. 1). The numbers of electrons involved in the reduction was determined to be almost one from the slope of this plot. Thus, each low-spin $(t_{2g})^5$ ruthenium(III) complex was found to undergo a ready one-electron reduction, which might be regarded as completing the metal t_{2g} subshell. In each case, the reciprocal slope of the logarithmic plot is (60±2) mV, indicating that the electrode reaction is a reversible step, with a one-electron transfer. The half-wave potentials measured in solutions of pH 5.0—7.5 and at an ionic strength of 0.1 mol dm^{-3} are almost constant; they are given in Table 1. However, the half-wave potentials shifted slightly in a positive direction with a lowering of the pH of the solution, as is exemplified in Fig. 1. This fact may be attributable to the increase in the reversibility of the electrode reaction resulting from the stabilization of the reduced Ru(II) species.

The redox potential of the Ru(III)/Ru(II) couple for the complexes of the $[Ru(O_2CR)(NH_3)_5]$ type shifts in a negative direction in this ligand order: $O_2CCCl_3 < O_2CCHCl_2 \approx O_2CCH_2F < O_2CCH_2Cl \approx O_2CCH_2Br \approx O_2CCH_2I < O_2CH < O_2CCH_2NH_2 <$

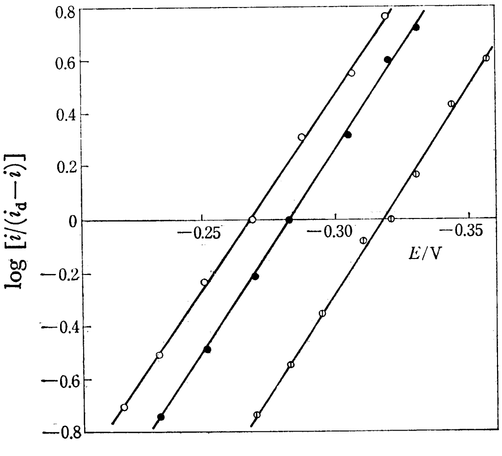

Fig. 1. Plots of $\log[i/(i_d-i)]$ *vs.* $E_{d.e.}$.
$[Ru(O_2CH)(NH_3)_5]^{2+}$, ○: 0.008 mol dm^{-3} *p*-toluene sulfonic acid, 0.092 mol dm^{-3} sodium *p*-toluenesulfonate, ●: 0.1 mol dm^{-3} sodium *p*-toluenesulfonate.
$[Ru(O_2CCH_2OH)(NH_3)_5]^{2+}$ ⦶: 0.1 mol dm^{-3} sodium *p*-toluenesulfonate.

$O_2CCH_2OH < O_2CCH_3 \approx O_2CC_2H_5 \approx O_2CCH(CH_3)_2$. This order agrees with that for the increasing pK_a values of the ligand acids, except for the glycinato complex.

When the complex ion reacts with the electrode as a depolarizer, the reduction is regarded as comprising the acceptance of an electron into the lowest unoccupied orbital of the complex. For the reduction process, the rate and mechanism of the overall process will be dictated by the localization and energy of the lowest orbital.[12] The Ru(III) complex with an electronic configuration of $(t_{2g})^5$ tends to take the $(t_{2g})^6$ configuration because of the high electron affinity of the unoccupied orbital, partly filled with one electron. Thus, the values of the redox potentials measured in this experiment are correlated with the energy level of the lowest unoccupied orbital of Ru(III) in the coordination sphere of pentaamminecarboxylato complexes.

Electronic Spectra of Ru(III) Complexes. The electronic spectra of all the complexes measured in a solution of 0.1 mol dm^{-3} *p*-toluenesulfonate at 25 °C exhibit an intense band in the energy region from 34.6×10^3 cm^{-1} to 33.6×10^3 cm^{-1}, as is shown in Table 1. These bands are assigned to the charge-transfer transition from ligand pπ to Ru(III) dπ orbitals on the basis of their intensity and spectral energies, and on the basis of a comparison of these data with those of the other related complexes.[13] The pπ-dπ charge-transfer energy in $[Ru^{III}O_2CR(NH_3)_5]$ complexes regularly decreases upon R-substituents of RCO_2 ligands in this order: $O_2CCCl_3 > O_2CCHCl_2 > O_2CCH_2F > O_2CCH_2Cl > O_2CCH_2Br \approx O_2CCH_2I > O_2CH \approx O_2CCH_2OH > O_2CCH_3 \approx O_2CC_2H_5 > O_2CCH(CH_3)_2 > O_2CCH_2NH_2$. This order agrees with that of the increasing pK_a values of the ligand acids except for the case of iso-butyric acid and glycine (Table 1).

It is of interest to examine whether or not there exists a direct relationship between the electrochemical stabilization of Ru(III) towards cathodic reductions, as expressed in terms of $E_{1/2}$ values, and the LMCT spectral energies. The plots of $E_{1/2}$ *vs.* ν_{max} (LMCT) are approximately linear for various pentaamminecarboxylatoruthenium(III) complexes, as is shown in Fig. 2. A linear relationship between the formal redox potential and the absorption maximum of the metal to ligand charge-transfer (MLCT) has been found to exist for various benzonitrile and pyridine complexes of Ru(II).[8] The charge-transfer energy is related only to the energy difference between pπ and dπ orbitals. On the contrary, the reversible half-wave potential is directly related to the energy level of a singly occupied dπ orbital. Therefore, this dπ orbital energy level may be a determinant factor for both the redox potential and the charge-transfer energy for pentaammine-carboxylatoruthenium(III) complexes.

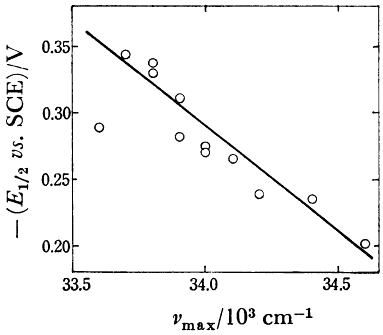

Fig. 2. Plot of half-wave potential $E_{1/2}$ of the $Ru(O_2CR)(NH_3)_5^{2+/+}$ couples *vs.* the wave number of the ligand-to-metal charge-transfer maxima for the $Ru(O_2CR)(NH_3)_5^{2+}$ complexes.

TABLE 1. HALF-WAVE POTENTIALS AND OPTICAL PARAMETERS OF PENTAAMMINERUTHENIUM(III) COMPLEXES AND DISSOCIATION CONSTANTS OF LIGAND ACIDS

Complex ion	$-(E_{1/2}$ *vs.* SCE)[a] / V	ν_{max} / 10^3 cm^{-1}	ε[b]	pK_a of ligand acid[c] (Ionic strength / mol dm^{-3})
$Ru(O_2CCCl_3)(NH_3)_5^{2+}$	$0.20_2 \pm 0.01$	34.6 ± 0.1	1380	0.635(0.003—0.01)
$Ru(O_2CCHCl_2)(NH_3)_5^{2+}$	$0.23_5 \pm 0.01$	34.4 ± 0.1	1490	1.257(0.001—0.2)
$Ru(O_2CCH_2F)(NH_3)_5^{2+}$	$0.23_8 \pm 0.01$	34.2 ± 0.1	1470	2.586(0.0003—0.0015)
$Ru(O_2CCH_2Cl)(NH_3)_5^{2+}$	$0.26_6 \pm 0.01$	34.1 ± 0.1	1510	2.854(0.0001—0.03)
$Ru(O_2CCH_2Br)(NH_3)_5^{2+}$	$0.27_0 \pm 0.02$	34.0 ± 0.1	1300	2.902(0.0003—0.001)
$Ru(O_2CCH_2I)(NH_3)_5^{2+}$	$0.27_5 \pm 0.02$	34.0 ± 0.1	710	3.175(0.0001—0.001)
$Ru(O_2CH)(NH_3)_5^{2+}$	$0.28_2 \pm 0.01$	33.9 ± 0.1	1540	3.752(0.01—0.2)
$Ru(O_2CCH_2OH)(NH_3)_5^{2+}$	$0.31_1 \pm 0.01$	33.9 ± 0.1	1480	3.831(0.005—0.08)
$Ru(O_2CCH_3)(NH_3)_5^{2+}$	$0.33_1 \pm 0.02$	33.8 ± 0.1	1590	4.756(0.01—0.2)
$Ru(O_2CCH_2CH_3)(NH_3)_5^{2+}$	$0.33_8 \pm 0.01$	33.8 ± 0.1	1660	4.874(0.01—0.09)
$Ru(O_2CCH(CH_3)_2)(NH_3)_5^{2+}$	$0.34_3 \pm 0.01$	33.7 ± 0.1	1770	4.862(0.01—0.02)
$Ru(O_2CCH_2NH_2)(NH_3)_5^{2+}$	$0.28_8 \pm 0.02$	33.6 ± 0.1	1560	2.350(0.01—0.36)

a) Supporting electrolyte solution: 0.1 mol dm^{-3} sodium *p*-toluenesulfonate.
b) mol^{-1} dm^3 cm^{-1}. c) From Ref. 11.

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