Electrochemistry of Tris(β-diketonato)ruthenium(III) Complexes at Platinum Electrodes in Nonaqueous Solutions and Substituent Effects on Their Reversible Half-Wave Potentials[1,2]

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(Received September 10, 1988)

The one-electron oxidation and reduction processes at platinum electrodes of a series of β-substituted and γ-substituted tris(β-diketonato)ruthenium(III) complexes are studied in acetonitrile, *N*,*N*-dimethylformamide, and nitromethane solutions, each containing 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C. Syntheses of three new γ-substituted derivatives are described. Attempts to isolate the immediate product of the one-electron oxidation of [Ru(acac)$_3$] in acetonitrile failed; bis(acetonitrile)bis(acetylacetonato)ruthenium(III) was obtained instead. Diffusion coefficients of the complexes in the acetonitrile medium are presented. The reversible half-wave potentials for the oxidation and the reduction in the acetonitrile medium depended linearly on the sum of the Hammett constants of the substituents (σ_p for the β-substituents and σ_m for the γ-substituents). Analysis of the dependence of the half-wave potentials on several kinds of substituent parameters suggests that the inductive effect is operative at both the β-positions and the γ-position, while the resonance effect is operative only at the β-positions.

Electrochemical properties of tris(β-diketonato)complexes involving many kinds of metals (e.g., cobalt(III),[3-7] chromium(III),[4,5,8,9] europium(III),[5] cerium(III),[5,6] iron(III),[4-6,9-12] manganese(III),[4-6,13] ruthenium(III),[14-18] and osmium(III)[15]) have been studied in various solvents. Most of these complexes undergo simple one-electron reduction and/or one-electron oxidation. In some cases, the reversible half-wave potentials for the reduction have been found to be linearly correlated with σ_p, σ_m, and σ^*, where σ_p and σ_m are the Hammett constants for para and meta positions, respectively, and σ^* is Taft's polar substituent constant.

Reduction processes of some tris(β-diketonato)ruthenium(III) complexes to the corresponding ruthenium(II) complexes have been studied in acetonitrile (AN)[14-18] and in *N*,*N*-dimethylformamide (DMF).[15] Linear relationships between the half-wave potentials and the sum of the Hammett constants were also reported.[15,18] These complexes, however, were all β-substituted complexes with one exception, and only a few quantitative analyses of oxidation processes to the ruthenium(IV) state have been reported.[14,16,19-21]

This paper deals with the electrochemical reduction and oxidation processes at platinum electrodes of a series of both β-substituted and γ-substituted tris(β-diketonato)ruthenium(III) complexes in AN, DMF, and nitromethane (NM). The electrochemistry in AN is studied in detail, since the potential window of AN, particularly its anodic limit for platinum electrodes, is wider than those of the other solvents. Substituent effects on the half-wave potentials for both the oxidation and the reduction are examined in terms of σ_p and σ_m. The diffusion coefficients of the complexes in AN are presented together with the partial molar volumes of a few related complexes.

Experimental

Preparation of the Ruthenium(III) Complexes.** All the tris(β-diketonato)ruthenium(III) complexes except **12**, **13**, and **14** were synthesized according to the "ruthenium blue solution" method.[22,23] The three halogenated complexes were prepared by the direct substitution at the γ-positions of the ligands of **9**. In the cases of **12** and **13**, a chloroform solution of *N*-bromosuccinimide (Wako Pure Chemical Ltd.) or *N*-chlorosuccinimide (Aldrich Chemical Company Inc.) was added to **9** dissolved in chloroform. In the case of **14**, a benzene solution of *N*-iodosuccinimide (Fluka AG) was added to a benzene solution of **9**, because preliminary experiments indicated that extended refluxing in chloroform led to complete decomposition of all the complex species. The amount-of-substance ratio of the *N*-halosuccinimide to **9** was 4.5 for **12**, 3.0 for **13**, and 9.0 for **14**. Too large an excess of the succinimide resulted in the decomposition of the product in the cases of **12** and **13**. *N*-Bromosuccinimide immediately reacted with **9** to give **13**. However, **12** was obtained by allowing the mixture to stand overnight, and **14** was obtained by refluxing the mixture for ca. 2 h. The solution containing the product was passed through a column of Merck Aluminiumoxid 90 (in the case of **12**, it was necessary to evaporate off the solvent and to extract the residue with benzene before the chromatographic separation). The eluent was evaporated to dryness. The residue was recrystallized from ethanol, and the crystals were dried under a vacuum. Interestingly, when the benzene solution of iodine monochloride was introduced to the benzene solution of **9**, the γ-chloro complex, not the γ-iodo complex, was produced immediately with ca. 100% yield, although this

** The ligand symbols are given in Table 1; the complexes are numbered as indicated there.

Table 1. Ligand Symbols[a] and Numbers for the Complexes

Number	Complex	[O=CR-CR'-CR''=O]⁻ R	R'	R''
β-Substituted complexes				
1	[Ru(fhfa)$_3$]	CF_3	H	CF_3
2	[Ru(fhoa)$_3$]	CF_3	H	C_4H_3O[a]
3	[Ru(bhfa)$_3$]	CF_3	H	C_6H_5
4	[Ru(fhsa)$_3$]	CF_3	H	C_4H_3S[a]
5	[Ru(fhma)$_3$]	CF_3	H	CH_3
6	[Ru(fhpa)$_3$]	CF_3	H	$C(CH_3)_3$
7	[Ru(bhba)$_3$]	C_6H_5	H	C_6H_5
8	[Ru(bhma)$_3$]	C_6H_5	H	CH_3
9	[Ru(acac)$_3$]	CH_3	H	CH_3
10	[Ru(mhpa)$_3$]	CH_3	H	$C(CH_3)_3$
11	[Ru(phpa)$_3$]	$C(CH_3)_3$	H	$C(CH_3)_3$
γ-Substituted complexes				
12	[Ru(mClma)$_3$]	CH_3	Cl	CH_3
13	[Ru(mBrma)$_3$]	CH_3	Br	CH_3
14	[Ru(mIma)$_3$]	CH_3	I	CH_3
15	[Ru(mbma)$_3$]	CH_3	C_6H_5	CH_3
16	[Ru(mmma)$_3$]	CH_3	CH_3	CH_3
17	[Ru(mema)$_3$]	CH_3	C_2H_5	CH_3
Mixed-ligand complexes				
18	[Ru(acac)$_2$(bhfa)][20,35]			
19	[Ru(acac)$_2$(fhfa)][20]			
20	[Ru(acac)$_2$(mClma)]			

a) These provisional symbols (except the usual "acac") are constructed as follows: the first and the penultimate letters represent R and R''; the middle R'; the last "a" means a derivative of acetylacetone; "b" stands for phenyl, "e" for ethyl, "f" for trifluoromethyl, "h" for hydrogen, "m" for methyl, "o" for 2-furyl, "p" for *t*-butyl, and "s" for 2-thienyl.

compound is known to be an iodination reagent in chloroform or in acetate buffer.[24] When a small amount of chloro-, bromo-, or iodosuccinimide was added to **9**, a mixture of the mixed-ligand complexes [Ru(acac)$_n$(mXma)$_{3-n}$] (X=Cl, Br, I) was formed. These mixed-ligand complexes may be separated by column chromatography. Actually, **20** was obtained in this way.

The three γ-halogenated complexes are new compounds. They are readily soluble in benzene and chloroform giving reddish blue solutions; they are sparingly soluble in acetonitrile and acetone. Their elemental analyses and other characteristics are as follows. **12** Found: Ru, 20.1; C, 37.1; H, 3.6%. Calcd for $RuC_{15}H_{18}O_6Cl_3$: Ru, 20.1; C, 35.9; H, 3.6%. **13** Found: Ru, 14.9; C, 27.3; H, 2.7%. Calcd for $RuC_{15}H_{18}O_6Br_3$: Ru, 15.9; C, 28.4; H, 2.9%. **14** Found: Ru, 12.0; C, 23.5; H, 2.3%. Calcd for $RuC_{15}H_{18}O_6I_3$: Ru, 13.0; C, 23.3; H, 2.3%. UV (AN; λ_{max}/nm with log [ε/mol^{-1} dm^3 cm^{-1}] in the parentheses): **12** 563 (3.36), 362 (3.95), 287 (4.15); **13** 556 (3.39), 363 (3.94). 291 (4.09); **14** 563 (3.44), 367 (3.92), 291 (4.08). ^{1}H NMR (C_6D_6): **12** δ=−8.31; **13**, δ=−7.79; **14**, δ=−7.16. Magneton number (μ_{eff}/μ_B): **12** 1.79; **13** 1.76; **14** 1.73.

All the complexes have optical isomers, and those complexes with three asymmetrical ligands have geometrical isomers. The samples used in the present experiment were mixtures of the isomers as prepared. No differences in the electrochemical behavior of the geometrical isomers were discernible.

Other Chemicals. Tris(acetylacetonato)iron(III) and tris(acetylacetonato)cobalt(III) were purified by sublimating the samples purchased from Dojindo Laboratories under a reduced pressure at ca. 180 °C and ca. 200 °C, respectively. The sample of [Fe(phpa)$_3$] was prepared according to Hammond et al.[25] and purified by sublimation at ca. 200 °C; the same procedure was used for preparing [Fe(mbma)$_3$], except that the ligand was dissolved in ethanol instead of methanol and the sample was purified by recrystallization from benzene–petroleum ether.

Tetraethylammonium perchlorate (TEAP), tetrabutylammonium perchlorate (TBAP), and tetrabutylammonium tetrafluoroborate ((TBA)BF_4) used as supporting electrolytes were of special polarographic grade purchased from Nakarai Chemicals, Ltd. Silver perchlorate was prepared by dissolving silver oxide in perchloric acid (this silver oxide was obtained by adding a sodium hydroxide solution to a silver nitrate solution). The mixture was evaporated to dryness. The anhydrous salt was obtained by drying the residue under vacuum at room temperature for ca. 24 h, and then at 50 °C for a few days. The purification method of acetonitrile[26] was slightly modified: the third distillation with calcium hydride was carried out under argon atmosphere by means of a Widmer-type distilling column (ca. 100 cm long). *N*,*N*-Dimethylformamide was spectral reagent grade (Dojindo Laboratories, Dotite Spectrosol). Nitromethane was purified according to the literature method.[27] The other chemicals were of guaranteed reagent grade.

Measurement. Two kinds of platinum test electrodes were used in the voltammetric experiments. One was a platinum disk electrode (PtDE) of 1.99 mm diameter embedded in glass, which was used for the cyclic and normal pulse voltammetry. The other was a rotating platinum disk electrode (RPtDE) of 1.96 mm diameter embedded in poly(tetrafluoroethylene). Both electrodes were polished with aluminium oxide (particle size, ca. 0.03 μm).

A platinum gauze electrode was used as the working electrode for controlled potential electrolysis. An MCI AS01 hanging mercury electrode (Mitsubishi Chemical Industries, Ltd.) was used for the chronoamperometric determination of diffusion coefficients. In all the experiments, a spiral of platinum wire or a sheet of platinum was used as an auxiliary electrode.

Silver–silver ion reference electrodes were used for all the solvents: a spiral of silver wire was immersed in the respective solvent containing 0.1 mol dm^{-3} $AgClO_4$. The $AgClO_4$ solution was freshly prepared at each experiment. The reference electrode was placed in a compartment of an H-type cell with a G4 glass frit plug. It was connected to the test solution through a bridge filled with 0.1 mol dm^{-3} TEAP, TBAP, or (TBA)BF_4 solution of the needed solvent. All the potential values in this report are referred to these electrodes.

The concentration of the supporting electrolyte was 0.1 mol dm^{-3}. All the electrochemical measurements were carried out at (25.0±0.1) °C. Deoxygenation of the solutions was carried out with argon gas which had been passed through a series of two washing bottles containing the needed solvent kept at 25 °C. A Fuso Polarograph Model 312 was used for normal pulse voltammetry. For cyclic voltammetry, a Fuso Potential Scanning Unit Model 321 was attached to this instrument. When the voltammetry was performed with RPtDE, a Nikko Keisoku Motor Speed Controller SC-5 was used.

The reversible half-wave potentials ($E^{r}_{1/2}$) were determined from the normal pulse or hydrodynamic voltammograms by means of the conventional logarithmic plot method (natural logarithm was used) in Nernstian cases. In quasi-reversible cases, the reversible half-wave potentials were obtained by extrapolating the plots of $E+(RT/nF)\ln(I/(I_d-I))$ against E.[28]

Controlled potential electrolysis was carried out by using either the Polarograph Model 312 with a Fuso Coulometer Model 343 or a controlled potential electrolyzer with digital coulometer[29] constructed in this laboratory. The computerized data acquisition-processing system used for the chronoamperometric determination of diffusion coefficients was described elsewhere.[30]

The partial molar volumes were determined as follows. The densities (d) of acetonitrile solutions containing the complex to be studied at different molalities (m) were measured by means of a digital density meter (Anton Paar, DMA 60 with a DMA 602 cell). The cell temperature was controlled within ±0.003 °C. The density meter was calibrated with nitrogen and ultrapure deionized water at the beginning and the end of each day's measurements. When $(1+mM)/d$, where M is the molar mass of the complex, is plotted against m, the slope of the tangent of this curve at m gives the partial molar volume at m. In the present experiment, the plot was linear in every case, and the partial molar volume at infinite dilution was determined as the slope of the linear least squares regression.

Results and Discussion

The Reduction Process in AN. Each ruthenium(III) complex gave a well-defined reduction step on the normal pulse polarogram and a pair of cathodic and anodic peaks on the cyclic voltammogram in 0.1 mol dm^{-3} TEAP–acetonitrile solution. In some cases, the reduction step was followed by a second step, which was partly covered by the final discharge of the base solution. Only the first steps will be discussed.

In every case, the limiting current of the first reduction step of the normal pulse voltammogram was diffusion controlled as indicated by the inversely proportional dependence of the limiting current on the square root of the sampling time. The logarithmic plot of the step was a straight line with a reciprocal slope near the Nernstian value for a one-electron step (RT/F=25.7 mV at 25 °C), except in the cases of **10**, **11**, **16**, and **17**, which had the most negative half-wave potentials. The logarithmic plots of these four complexes were curved, indicating that their reduction processes were quasi-reversible at the platinum electrode, whereas their reduction processes were Nernstian at mercury electrodes. The peak separations of the cyclic voltammograms (ΔE_p) reflected this situation. These data are presented in Table 2. The reversible half-wave potentials of the reduction at PtDE for all the complexes were in good agreement with those observed at a dropping mercury electrode.

At RPtDE, all the complexes except the above-mentioned four complexes showed Nernstian steps over the rotation frequency range between 400 min^{-1} and 3600 min^{-1}. The limiting currents were convective-diffusion-controlled. The voltammograms of **10** and **11** showed Nernstian steps only at lower rotation frequencies. The reduction steps of **16** and **17** were poorly reproducible even at lower rotation frequencies.

The Reduction Processes in DMF and NM. The following five complexes were examined: **1**, **5**, **8**, **9**, and **11**. In 0.1 mol dm^{-3} TEAP–DMF solution, **5** and **8** gave Nernstian reduction steps at PtDE, as indicated by the ΔE_p values (Table 3) and the reciprocal slopes of the logarithmic plots of the normal pulse voltammograms (not listed). However, the reduction processes of **9** and **11** were quasi-reversible at PtDE, although Patterson and Holm[15] reported that the reductions at a platinum electrode were Nernstian in DMF. The data for **1** in DMF were obtained from the quasi-reversible oxidation step observed with a test solution containing K[Ru(fhfa)$_3$], because **1** was quickly reduced to the ruthenate(II).

In 0.1 mol dm^{-3} TEAP–NM solution, **1**, **5**, and **8** showed quasi-reversible reduction steps at PtDE, while no reduction steps of **9** and **11** were observed within the potential window of this medium.

The reversibility of the reduction processes of the tris(β-diketonato)ruthenium(III) complexes depended on both the kind of solvent and the electrode material. Nevertheless, the relative values of $E^{r}_{1/2}$ in each solvent (the values referred to **8** are given in Table 4) were almost independent of the kind of solvent. The

Table 2. Electrochemical Data of β-Diketonatoruthenium(III) Complexes[a,b]

Complex	$\Sigma\sigma_{pmp}$	Ru^{IV}/Ru^{III}			Ru^{III}/Ru^{II}			$10^{10}D$	r_S
		ΔE_p/mV	s/mV	$E^r_{1/2}$/V	ΔE_p/mV	s/mV	$E^r_{1/2}$/V	$m^2\,s^{-1}$	nm
β-Substituted complexes									
1	+3.24	no	no	no	68	27.7	+0.36	11.8	0.510
2	+1.89	73	25.8	+1.22	65	25.1	−0.32	10.9	0.552
3	+1.59	75	qr	+1.21	67	29.3	−0.33	11.0	0.547
4	+1.59	69	25.3	+1.28	67	25.5	−0.33	10.8	0.558
5	+1.11	72	qr	+1.31	69	27.9	−0.45	15.0	0.401
6	+1.02	260	qr	+1.27[c]	60	26.5	−0.53	12.6	0.478
7	−0.06	59	25.8	+0.68	65	26.9	−0.88	7.8	0.772
8	−0.54	60	26.1	+0.66	64	26.5	−1.02	10.7	0.563
9	−1.02	61	25.8	+0.63	68	29.6	−1.14	14.5	0.415
10	−1.11	67	25.3	+0.60	78	qr	−1.21	11.7	0.515
11	−1.20	59	26.0	+0.46	80	qr	−1.44	11.6	0.519
γ-Substituted complexes									
12	+0.09	74	26.1	+0.80	65	25.6	−0.82	12.6	0.478
13	+0.15	70	24.6	+0.79	65	25.6	−0.81	12.2	0.494
14	+0.03	65	25.4	+0.73	65	25.8	−0.84	12.3	0.490
15	−0.84	59	25.5	+0.53	60	28.4	−1.21	10.4	0.579
16	−1.23	67	27.6	+0.35	67	qr	−1.30	13.2	0.456
17	−1.23	65	27.6	+0.35	80	qr	−1.34	12.4	0.486
Mixed-ligand complexes									
18[20]	−0.15	61	27.7	+0.84	65	26.9	−0.85		
19[20]	+0.40	70	25.1	+1.05	66	26.0	−0.61		
20	−0.65	68	28.1	+0.68	71	27.9	−1.03		

a) $E^r_{1/2}$, reversible half-wave potential vs. Ag/0.1 mol dm^{-3} $AgClO_4$ in AN; ΔE_p, cyclic voltammetric peak separation; D, diffusion coefficient; s, the absolute value of the reciprocal slope of the natural logarithmic plot; r_S, the Stokes radius calculated from the D value; no, not observed; qr, quasi-reversible. b) 1 mol m^{-3} in 0.1 mol dm^{-3} TEAP–AN at 25°C, PtDE. c) The values previously reported[2a,21] are revised.

Table 3. Peak Separations (ΔE_p) and Reversible Half-Wave Potentials ($E^r_{1/2}$)[a] for Ru^{IV}/Ru^{III} and Ru^{III}/Ru^{II} Steps of Some Tris(β-diketonato)ruthenium(III) Complexes at PtDE in DMF and NM Containing 0.1 mol dm^{-3} TEAP at 25°C

Solvent	DMF				NM			
	Ru^{IV}/Ru^{III}		Ru^{III}/Ru^{II}		Ru^{IV}/Ru^{III}		Ru^{III}/Ru^{II}	
Complex[b]	ΔE_p/mV	$E^r_{1/2}$/V	ΔE_p/mV	$E^r_{1/2}$/V	ΔE_p/mV	$E^r_{1/2}$/V	ΔE_p/mV	$E^r_{1/2}$/V
1	c)	c)	141[d]	+0.27[d]	c)	c)	85	−0.17
5	c)	c)	69	−0.54	c)	c)	92	−0.95
8	100	+0.56	67	−1.14	65	+0.14	78	−1.49
9	84	+0.53	100	−1.29	86	+0.16	c)	c)
11	102	+0.40	84	−1.56	79	−0.09	c)	c)

a) Against Ag/0.1 mol dm^{-3} $AgClO_4$ in the respective solvent. b) Concentration, 1 mol m^{-3}. c) Not observed. d) $K[Ru^{II}(fhfa)_3]$ was used (see text).

Table 4. Relative Reversible Half-Wave Potentials ($\Delta E^r_{1/2}$)[a] for Ru^{IV}/Ru^{III} and Ru^{III}/Ru^{II} Steps in AN, DMF, and NM Containing 0.1 mol dm^{-3} TEAP at 25°C

Complex	$\Delta E^r_{1/2}(Ru^{IV}/Ru^{III})$/V			$\Delta E^r_{1/2}(Ru^{III}/Ru^{II})$/V		
	AN	DMF	NM	AN	DMF	NM
1	b)	b)	b)	1.38	1.41	1.32
5	0.65	b)	b)	0.57	0.60	0.54
9	−0.03	−0.03	+0.02	−0.12	−0.15	b)
11	−0.20	−0.16	−0.23	−0.42	−0.42	b)

a) Referred to the $E^r_{1/2}$ value of [Ru(bhma)$_3$] (**8**) in each medium. b) Not observed.

solvent effects on the reversible half-wave potential for the reduction appear to be small, in spite of the difference in the donor numbers of these solvents.

Oxidation Process in AN. A well-defined oxidation step was observed at both PtDE and RPtDE, and the cyclic voltammogram at PtDE exhibited a corresponding pair of anodic and cathodic peaks for each complex, except in the case of **1**, which showed no oxidation step within the potential window. In most cases, this step was followed by an ill-defined, irreversible second oxidation step, which will not be discussed.

The first steps were diffusion controlled. Comparison of their diffusion currents to those of the first reduction steps indicated that they were one-electron steps. These steps were Nernstian, except for the three complexes with the most positive half-wave potentials, i.e., **3**, **5**, and **6**. The oxidation steps of these three complexes were quasi-reversible. The $E^{I}_{1/2}$ values and the reciprocal slopes are presented in Table 2 together with the cyclic voltammetric ΔE_p values.

The constant potential coulometry of **8**, **9**, **11**, and **15** in AN confirmed that the steps were of the one-electron oxidation process to the corresponding ruthenium(IV) species and that the ruthenium(IV) complexes were stable and could be electrolytically reduced to the original ruthenium(III) species in a quantitative way.

In some other cases, however, the oxidation process was accompanied by slow subsequent reactions. When **3** was electrolyzed at +1.5 V in 0.1 mol dm^{-3} TEAP–AN, the anodic diffusion current decreased only slightly with the progress of the electrolysis, and the reduction step of $[Ru^{IV}(bhfa)_3]^+$ did not appear. Instead, new steps appeared at more negative potentials. Similar phenomena were observed when the supporting electrolyte was (TBA)BF_4 or TBAP. These facts show that the most part of $[Ru^{IV}(bhfa)_3]^+$ was reduced back to **3** by some species, whose oxidation product(s) produced the new reduction steps. Such regenerative reduction of the ruthenium(IV) species was observed also in the cases of **2**, **5**, and **6**. The oxidized forms of the complexes with $E^{I}_{1/2}(Ru^{IV}/Ru^{III})$ values more positive than +1.2 V catalyzed the oxidation of some unidentified species. These catalytic oxidation processes were fast enough to be observed in the controlled potential electrolysis, but they were too slow to affect the voltammetric current–voltage curves.

Since the oxidized forms of those complexes with less positive half-wave potentials (**9**, **11**, **15**, etc.) were stable in the acetonitrile solution, as mentioned above, attempts were made to isolate the ruthenium(IV) species. A blue solution which was obtained by the electrolytic oxidation of **9** in the $NaClO_4$–AN solution was evaporated under a reduced pressure. The residue was extracted with benzene. A blue solid was obtained when the benzene extract was evaporated. These operations were carried out under an argon atmosphere, and care was taken to exclude moisture as far as possible.

This blue solid was $[Ru^{III}(acac)_2(CH_3CN)_2](ClO_4)$ as indicated by the elemental analyses: Found: C,33.5; H, 4.0; N, 5.7% (Calcd for $RuC_{14}H_{20}N_2O_8Cl$: C, 35.0; H, 4.2; N, 5.7%), although the UV-vis spectrum of its $NaClO_4$–AN solution (λ_{max}/nm=285, 322, 580) was almost the same as that of the original solution from which it had been separated (λ_{max}/nm=280, 323, 560). This compound in the AN medium showed a reversible reduction step with $E^{I}_{1/2}$=−0.24 V, which agreed well with the half-wave potential of the oxidation step of $[Ru^{II}(acac)_2(CH_3CN)_2]$.[31] Its other characteristics are as follows: IR (KBr) 1095 cm^{-1} (ClO_4^-), 2300 cm^{-1} (CH_3CN). Magneton number, 1.75.

In this way, $[Ru^{IV}(acac)_3]^+$ was converted to the bis(acetonitrile) complex in the course of isolation. Attempts at isolating the oxidized products of **11** and **15**, which were also found to be stable in the acetonitrile solution, have so far led to recovering the original ruthenium(III) complexes. It appears that these tris(β-diketonato)ruthenium(IV) species were stable only in the presence of acetonitrile, and that their isolation would be very difficult, if not impossible, although a number of mononuclear ruthenium(IV) species with O^{2-}, halide ions, pyridine, or other organic ligands have been isolated.[19,32]

Oxidation Processes in DMF and NM. Five complexes, **1**, **5**, **8**, **9**, and **11**, were examined in these media. Among them, **8**, **9**, and **11** showed quasi-reversible one-electron oxidation steps (Table 3). The oxidation steps of the complexes with trifluoromethyl substituents lay beyond the positive ends of the potential windows of these media. Here again, the relative values of $E^{I}_{1/2}$ were roughly the same in the three solvents (Table 4).

Diffusion Coefficients and Partial Molar Volumes. The values of the diffusion coefficients of the tris(β-diketonato)ruthenium(III) complexes were evaluated approximately on the basis of the Levich equation from both the oxidation and the reduction limiting currents at the RPtDE, with the following values for 0.1 mol dm^{-3} TEAP–AN solution at 25 °C: density, 0.7901 g cm^{-3} and viscosity, 3.627×10^{-3} g cm^{-1} s^{-1}. For each complex, the value of the diffusion coefficient calculated from the oxidation limiting current agreed well with that calculated from the reduction limiting current. These values are listed in Table 2.

In order to establish the validity of these values, a more accurate value of the diffusion coefficient of **9** was determined by means of the chronoamperometric method with hanging mercury drop electrode[33] at several potentials in the cathodic diffusion current region. The average value obtained from four independent data sets (each consisting of at least six

Table 5. Partial Molar Volumes of Some Tris(β-diketonato) Complexes in Acetonitrile

t/°C	V_m/cm³ mol⁻¹				
	[Fe(acac)₃]	[Fe(mbma)₃]	[Fe(phpa)₃]	[Co(acac)₃]	[Ru(acac)₃]
15	272.2			257.4	264.1
20	274.3				
25	275.0		585.2	259.9	261.6
30	283.3				
35	269.0	457.8	590.3	259.5	269.8
Average[a]	274.2±1.3	457.8±1.0	588.2±2.5	258.0±0.6	263.4±1.2
N	18	4	7	12	12
V_c[b]	261[36]		571[37]	253[38]	251[39]

a) Calculated from the pooled N measurements over all the temperature; the uncertainty is the standard deviation.
b) Molar volume of crystal/cm³ mol⁻¹.

chronoamperograms) was (14.4±0.3)×10⁻¹⁰ m² s⁻¹ at 95% confidence level. The agreement between this value and the value in Table 2 is satisfactory.

The complexes with more bulky ligands seem to have smaller diffusion coefficients. Table 2 includes the Stokes radii calculated from the D values on the basis of the Einstein-Stokes relation. The partial molar volume (V_m) of **9** in AN (not containing the supporting electrolyte) was determined and is presented in Table 5 together with the values for some other tris(β-diketonato) complexes. The averages were calculated by pooling the data over all the temperatures, because the variations of V_m with temperature were within the experimental errors. It is seen that the V_m values are slightly larger than the molar volumes of the crystals.

The radius of a sphere having the same volume as the V_m/L value (L is the Avogadro constant) of **9** is 0.471 nm, and the radius calculated on the basis of the molar volume of the crystal is 0.463 nm. The Stokes radius of **9** is smaller than these values. Such a "negative effect" is reported in the cases of tetraalkylammonium perchlorate, and other bulky polyatomic ions.[34]

Substituent Effect on $E^r_{1/2}$. The values of $E^r_{1/2}$(Ru^{III}/Ru^{II}) and $E^r_{1/2}$(Ru^{IV}/Ru^{III}) in AN are listed in Table 2; the data for some mixed ligand complexes are also included. The values depended on the substituents of the ligands: with the increase in the number and/or the strength of electron-withdrawing substituents, both $E^r_{1/2}$(Ru^{III}/Ru^{II}) and $E^r_{1/2}$(Ru^{IV}/Ru^{III}) became more positive. Patterson and Holm[15] investigated the substituent effect on $E^r_{1/2}$(Ru^{III}/Ru^{II}) at platinum electrode in DMF of a series of β-substituted tris(β-diketonato)ruthenium(III) complexes, which included eight of the present ones. They found linear relationships between $E^r_{1/2}$(Ru^{III}/Ru^{II}) and the sums of Hammett constants or Taft constants. We have also reported a similar linear relationship for the reduction at mercury electrodes in AN.[18]

A more detailed study of the substituent effect is feasible now that quite a number of the β-substituted and γ-substituted derivatives have become available. Here, the effect of the substituents at the β- and γ-positions on the reversible half-wave potentials for the reduction and the oxidation is examined in terms of the following combinations of σ_m, and σ_p, where σ_m and σ_p are the Hammett constants for the meta and the para positions of the specified substituents.

$$\Sigma\sigma_{mmm} = 3[\sigma_m(R) + \sigma_m(R') + \sigma_m(R'')] \quad (1)$$

$$\Sigma\sigma_{mpm} = 3[\sigma_m(R) + \sigma_p(R') + \sigma_m(R'')] \quad (2)$$

$$\Sigma\sigma_{pmp} = 3[\sigma_p(R) + \sigma_m(R') + \sigma_p(R'')] \quad (3)$$

$$\Sigma\sigma_{ppp} = 3[\sigma_p(R) + \sigma_p(R') + \sigma_p(R'')] \quad (4)$$

Linear regression lines are drawn through the plots of $E^r_{1/2}$(Ru^{III}/Ru^{II}) and $E^r_{1/2}$(Ru^{IV}/Ru^{III}) against these parameters (the plots against $\Sigma\sigma_{pmp}$ are presented in Fig. 1). The plots against $\Sigma\sigma_{mpm}$ and $\Sigma\sigma_{pmp}$ fit to straight lines better than the others, mainly because the points for the γ-substituted complexes tend to deviate from the regression line for the β-subsituted complexes if $\Sigma\sigma_{mmm}$ or $\Sigma\sigma_{ppp}$ is taken as the parameter.

Whether $\Sigma\sigma_{mpm}$ or $\Sigma\sigma_{pmp}$ is more reasonable, however, cannot be decided by the fitness of the regressions. A more detailed piece of information is obtained when the relationships of $E^r_{1/2}$ with Taft's inductive substituent constant σ_I and the resonance substituent constant σ_R^0 are examined, because σ_p is a parameter which pertains to both the inductive and resonance effects.

When the $E^r_{1/2}$ values are plotted against $\Sigma\sigma_I$, two pairs of straight lines can be drawn: one for the β-substituted complexes and the other for the γ-substituted complexes (Fig. 2). This fact indicates that the inductive effect of the substituent strongly affects $E^r_{1/2}$ both at the β-position and at the γ-position. But, the slopes of the lines for the γ-substituents is smaller than those for the β-substituents, probably reflecting the γ-position's remoteness from the ruthenium atom.

When $E^r_{1/2}$ is plotted against $\Sigma\sigma_R^0$ (Fig. 3), an evident linear correlation is found only for the β-substituted complexes, while the points for the γ-substituted complexes are scattered. This fact

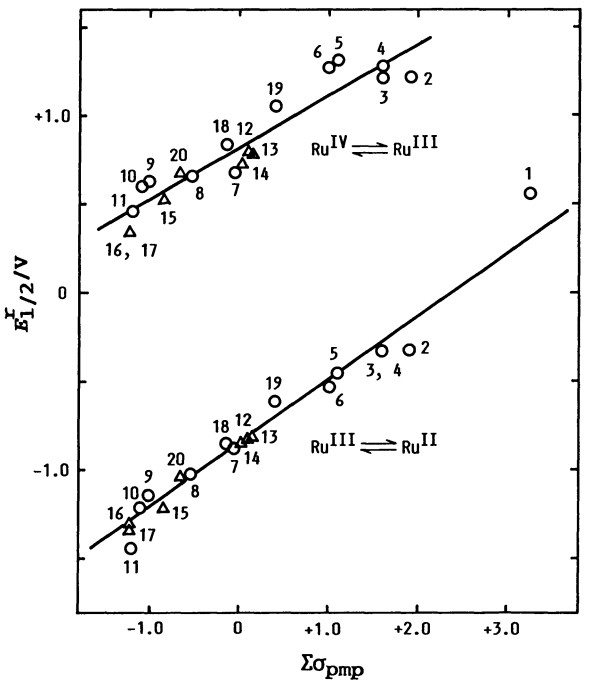

Fig. 1. Plots of $E^{I}_{1/2}$ against $\Sigma\sigma_{pmp}$.
Slope(Ru^{IV}/Ru^{III})=0.293 V, correlation coefficient-(Ru^{IV}/Ru^{III})=0.949; slope(Ru^{III}/Ru^{II})=0.354 V, correlation coefficient(Ru^{III}/Ru^{II})=0.988.
O: β-Substituted complexes, Δ: γ-substituted complexes.

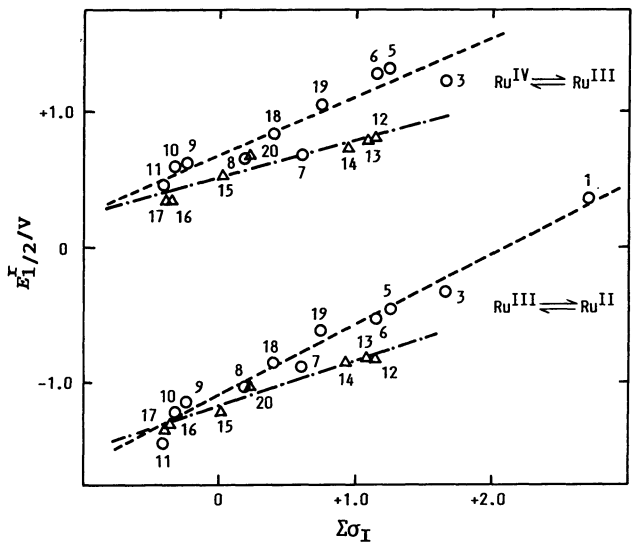

Fig. 2. Plots of $E^{I}_{1/2}$ against $\Sigma\sigma_{I}$.
---O---: β-Substituted complexes; slope(Ru^{IV}/Ru^{III})=0.407 V, correlation coefficient(Ru^{IV}/Ru^{III})=0.922; slope(Ru^{III}/Ru^{II})=0.523 V, correlation coefficient(Ru^{III}/Ru^{II})=0.988.
-·-Δ-·-: γ-Substituted complexes; slope(Ru^{IV}/Ru^{III})=0.280 V, correlation coefficient(Ru^{IV}/Ru^{III})=0.955; slope(Ru^{III}/Ru^{II})=0.345 V, correlation coefficient(Ru^{III}/Ru^{II})=0.986.

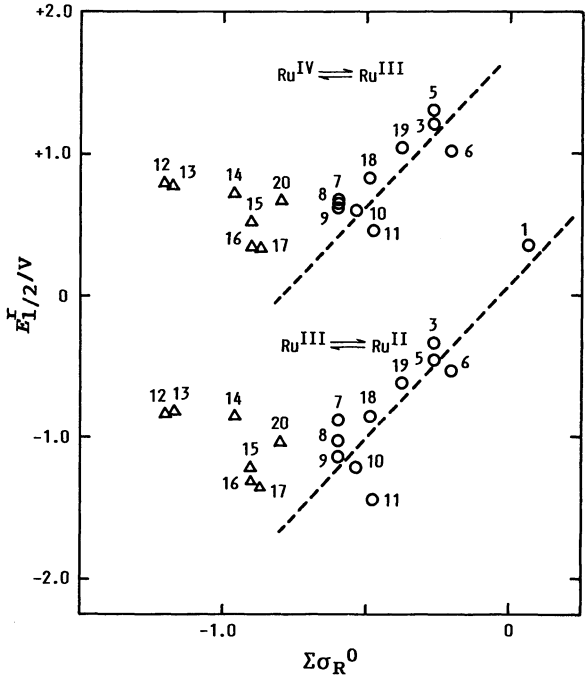

Fig. 3. Plots of $E^{I}_{1/2}$ against $\Sigma\sigma_{R}{}^{0}$.
---O---: β-Substituted complexes, Δ: γ-substituted complexes.

indicates that the resonance effect plays a less decisive role when the substituent is at the γ-position. In other words, the effect of the substituent at the γ-position is predominantly inductive, whereas the substituents at the β-positions exert both inductive and resoance effects. It is, therefore, $\Sigma\sigma_{pmp}$ that describes the substituent effects more reasonably than the other combinations of σ_p and σ_m. The same tendency has been observed in chromium(III) and cobalt(III) systems. In the case of tris(β-diketonato)chromium(III) complexes, Handy and Lindvedt[8] and Tsiamis et al.[9] established linear dependence of $E^{I}_{1/2}(Cr^{III}/Cr^{II})$ on $\Sigma\sigma_{pmp}$. With β-substituted tris(β-diketonato)cobalt-(III) complexes, the regression of the half-wave potential on $\Sigma\sigma_p$ was better than that on $\Sigma\sigma_m$.[3]

The substituent effects in β-diketonato ruthenium-(III) complexes have been explained qualitatively in terms of the influence of the substituents on the electron densities in the dπ orbitals.[15] The above-mentioned tendency has been accounted for by the idea that the β-substituents perturb the electron density on the ligating oxygen atoms rather than on the central atom.[8] Quantitative explanation is difficult, however, in the case of β-diketonato ruthenium-(III) complexes, which are paramagnetic, since no information about the electronic state is available directly from the UV-vis spectra, and the molecular orbital calculations are not easy.

The authors thank Makiko Ikai, Shinji Arai, and Noriko Mihara for their experimental assistance and

Dr. Yuichi Satsu for his helpful discussions. Dr. Kazuko Tanaka, The Institute of Physical and Chemical Research, kindly permitted the use of the digital density meter of her laboratory. Mrs. Nakako Tokita's assistance in the elemental analyses is gratefully acknowledged. Thanks are also due to Dr. F. Scott Howell, Sophia University, for correcting the manuscript. This work was partially supported by Grants-in-Aid for Scientific Research Nos. 547045 and 58740287 from the Ministry of Education, Science and Culture.

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