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The Reduction of [Ru(Hedta)(H_2O)] at the Mercury Electrode and Subsequent Reactions*

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The reduction of [Ru(Hedta)(H_2O)] at the mercury electrode and the subsequent chemical reactions in buffer solutions were investigated by AC and DC polarography and by large-scale electrolysis. Two polarographic steps were observed; the more positive step is discussed in this paper. The step was a diffusion-controlled, one-electron reduction of ruthenium(III) to ruthenium(II). For $[H^+]=(10^{-3}—10^{-5})$ mol dm^{-3} the reduction was reversible, and it became less reversible if $[H^+]<10^{-5}$ mol dm^{-3}. Large-scale electrolysis in formate buffer solutions at the potential of the polarographic diffusion current plateau confirmed that the reduction is a one-electron process. In formate buffer, the reduced form of the complex is deactivated. Furthermore, in the presence of perchlorate ions the reduced form is reoxidized to the original form. The rate constant for the reoxidation reaction at 25.0 °C was $k_2=(1.38\pm0.26)\times10^{-3}$ mol^{-1} dm^3 s^{-1}. The activation parameters for the reoxidation reaction were $\Delta H^{\neq}=(94.1\pm17.6)\times10^3$ J mol^{-1} and $\Delta S^{\neq}=(19.0\pm6.3)$ J K^{-1} mol^{-1}.

Although electrochemical studies of ruthenium have been reported by several authors,[1–7] most of the work dealt with aqua or chloro complexes in aqueous solutions. In fact, the electrode processes of ruthenium complexes are not well understood.

All the known complexes of ruthenium(II) and ruthenium(III) take the low-spin d^6 and d^5 configurations respectively, which are considerably substitution-inert. Taube and co-workers[8–11] first studied redox reactions of ammine complexes of ruthenium(II) and ruthenium(III) in aqueous solutions and proposed that the electron transfer process between them proceeds *via* an outer-sphere mechanism. They reported also that ruthenium(II) complexes can be oxidixed by perchlorate ions, which are known to be relatively weak oxidizing agents. Recently the oxidation of ruthenium(II) aqua complexes by perchlorate ions[12] and substitution reactions on ruthenium(II) complexes[13–16] have been reported, and these data are in agreement with those reported by Taube. Recent progress in the study of redox reactions of ruthenium complexes has been reviewed by Ford[17] and Taube.[18]

In the present work, (hydrogenethylenediaminetetraacetato)aquaruthenium(III), which has been proved to take the low-spin d^5 configuration,[19] was investigated by means of polarography, and the effect of perchlorate ions on the reduced form of the complex was investigated by using a large-scale electrolytic method.

Experimental

Materials. (Hydrogenethylenediaminetetraacetato)-aquaruthenium(III)-3-water, [Ru(Hedta)(H_2O)]·3H_2O was prepared according to the procedure described by Mukaida.[19] The product was a dull-yellow powder and readily soluble in water (Found: C, 25.73; H, 3.29; N, 6.18%. Calcd: C, 25.97; H, 4.59; N, 6.06%). The IR spectrum of the product obtained agreed with that reported by Mukaida. Its purity as determined by alkalimetric titration was 99.96%. The alkalimetric titration curve showed two pH-jumps indicating the existence of two dissociable protons. The p*K* values** calculated from the pH-titration curve were 2.37 and 7.63. This pK_1 value was very similar to that of [Rh(Hedta)(H_2O)] (pK_1=2.32, pK_2=9.12),[20] but the aqua group was more acidic than in the rhodium complex. The corresponding equilibria are represented by;

$$[\mathrm{Ru(Hedta)(H_2O)}] \xrightleftharpoons{K_1} [\mathrm{Ru(edta)(H_2O)}]^- + \mathrm{H}^+$$

$$[\mathrm{Ru(edta)(H_2O)}^-] \xrightleftharpoons{K_2} [\mathrm{Ru(edta)(OH)}]^{2-} + \mathrm{H}^+$$

The near ultraviolet-visible absorption spectrum of the complex in 0.2 mol dm^{-3} formic acid–sodium formate solution (pH=2.80) showed one absorption band at 283 nm ($\varepsilon=2.75\times10^2$ m^2 mol^{-1}). The spectrum remained identical in 0.01 mol dm^{-3} (pH=1.88) and 1.0 mol dm^{-3} (pH=0.88) perchloric acid solutions as well.

Sodium perchlorate-1-water was prepared from perchloric acid and sodium carbonate, according to the procedure reported earlier.[21]

All the other reagents were of Guaranteed Reagent grade and used without further purification. Twice distilled water was used except for the synthesis of the complex.

Polarography. All the polarograms were recorded with a potentiostat type AC-DC polarograph constructed locally. For AC polarography, alternating voltage of 10 mV (rms) was superimposed, the frequency was 35 Hz unless otherwise stated. The characteristics of the dropping mercury electrode (DME) were as follows: $m=1.685$ mg s^{-1}, $t_d=4.89$ s under a mercury head of 60 cm (−0.4 V *vs.* SCE, acetate buffer, ionic strength=0.5 mol dm^{-3}, 25.0 °C).

A conventional beaker type cell was used for polarographic measurements. A spiral of platinum wire served as the counter electrode. A reference saturated calomel electrode (SCE) was connected to the cell solution through a series of two H-type salt bridges (saturated sodium nitrate) with filter paper plugs. Dissolved oxygen was expelled by passing nitrogen which had been passed through vanadium(II) sulfate solution and water.

The following supporting electrolytes were used for the polarographic measurements: sodium acetate – acetic acid buffer (pH$_c$***$>$3.5), sodium formate – formic acid buffer ($2>$pH$_c>3.5$), 0.02 mol dm^{-3} sodium perchlorate – 0.18 mol dm^{-3} perchloric acid (pH$_c$=0.72). The ionic strength of all the buffer solutions was adjusted to 0.2 mol dm^{-3} with sodium perchlorate. Each solution contained 0.002% gelatin as maximum suppressor.

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** p*K* represents $-\log(K/\mathrm{mol\ dm^{-3}})$.

*** pH$_c$ represents $-\log([\mathrm{H^+}]/\mathrm{mol\ dm^{-3}})$.

All the potentials reported in this paper refer to SCE. All measurements were performed at (25.0±0.1)°C unless otherwise stated.

Controlled-Potential Electrolysis. The electrolytic measurement was performed with a potentiostat type electrolyzer constructed locally. About 20 μmol of the complex dissolved in 10 cm^3 of supporting electrolyte solution was electrolyzed at -0.40 V under a nitrogen atmosphere in a glass cell having two side compartments. The side compartments were separated from the cell by agar plugs. The working electrode was a mercury pool at the bottom of the cell (surface area, about 7.1 cm^2). Another mercury pool in one of the side compartments served as the counter electrode, and an SCE was connected to the solution in the other side compartment. The solution was stirred during electrolysis with a stirrer made of polyformaldehyde resin rotating at 700 revolutions per minutes. The cell was equipped with a DME for recording polarograms in the course of electrolysis. The quantity of electricity was determined by integrating the recorded electrolytic current-time curve graphically. The electrolytic current was corrected for the residual current.

For all electrolytic measurements, a mixture of sodium formate - formic acid was used as buffer, sodium perchlorate being added when perchlorate ion effect was studied. The ionic strength of the solutions was adjusted to 0.5 mol dm^{-3} by adding sodium chloride.

Others. Alkalimetric titration of the complex was performed with an automatic titrator (Radiometer; Type ASU1a Auto Burette, TTC1c Titrator, SBR2c Titrigraph). An appropriate amount of the complex was titrated with a carbon-dioxide free sodium hydroxide solution standardized against potassium hydrogenphthalate.

All the pH$_c$ values of the solutions were determined with a Radiometer pH Meter 25E, whose meter readings were calibrated against standard hydrochloric acid solutions, and the hydrogen ion concentrations of the solutions were directly calculated from their pH$_c$ values.

Results

Polarography. Typical AC and DC polarograms of [Ru(Hedta)(H$_2$O)] are shown in Fig. 1. Two DC steps appeared at -0.2 and -1.0 V. A symmetrical AC wave appeared at the potential of the more positive (first) step; but no AC wave corresponding to the more negative (second) step was observed. The heights of both DC steps were nearly equal, but the second step appeared to be less steep than the first and was accompanied by a maximum, which could not be suppressed even in the presence of 0.02% gelatin. The maximum became larger at higher hydrogen ion concentration, and no distinct second step was observed in formic acid - sodium formate buffer solutions. It was impossible to infer the nature of the first reduction product from the analysis of the second step.

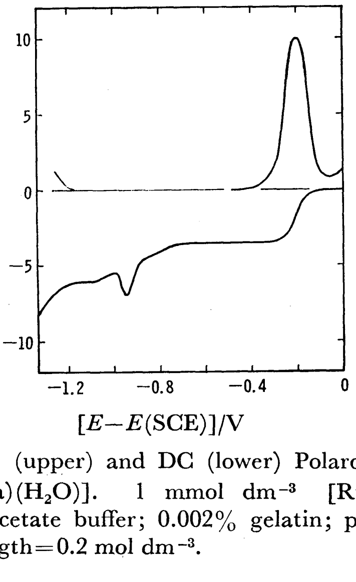


Fig. 1. AC (upper) and DC (lower) Polarograms of [Ru(Hedta)(H$_2$O)]. 1 mmol dm^{-3} [Ru(Hedta)(H$_2$O)]; acetate buffer; 0.002% gelatin; pH$_c$=3.68; ionic strength=0.2 mol dm^{-3}.

The limiting current of the first step was directly proportional to both the concentration of the complex and the square root of the corrected head of mercury. No kinetic contribution was detected even at 40.0 °C. The half-wave potential was affected neither by the concentration of the complex nor the drop time.

The plot of $\log[i/(i_d-i)]$ against E, where i_d and i are the diffusion current and the current at potential E, respectively resulted in a straight line whose reciprocal slope was -62—-63 mV at pH$_c$<5. At pH$_c$ higher than 5, the reciprocal slope was larger and increased gradually over a long period of time (a few hours at 25.0 °C), presumably owing to slow hydrolysis of the complex. The half-wave potential became more negative at higher pH$_c$, and tended to reach a constant value at pH$_c$ higher than 5 (Fig. 2). It was independent of free edta added to the solution up to 100 mmol dm^{-3} at pH$_c$=3.68.

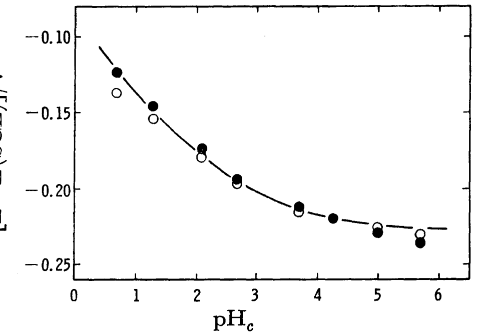


Fig. 2. pH$_c$-Dependence of half-wave potential and summit potential. 1 mmol dm^{-3} [Ru(Hedta)(H$_2$O)]; buffer solution; ionic strength=0.2 mol dm^{-3}; ●: $E_{1/2}$, ○: E_s, ——Calculation from Eq. (1b) using the best-fit set of K_O, K_R, and K'_R.

The polarographic diffusion coefficient of the complex (pH$_c$=3.68) calculated by using the Ilkovic equation modified by Koutecký[22] was 6.00×10^{-10} m^2 s^{-1}. This value is quite reasonable when compared with those of similar depolarizers obtained by the same method: (Cu(II)edta,[23] 5.47×10^{-10} m^2 s^{-1}; Tl(III)-edta,[24] 5.8×10^{-10} m^2 s^{-1}; H$_4$edta,[25] 5.01×10^{-10} m^2 s^{-1}).

The summit potential, E_s, of the corresponding AC wave coincided with $E_{1/2}$ within ±2 mV when the pH$_c$ of the solution was higher than about 2. At a lower pH$_c$, E_s became more negative than $E_{1/2}$ (Fig. 2).

When $\log[(i_s/i)^{1/2}-(i_s-i)/i^{1/2}]$ (where i_s and i are the alternating currents at E_s and at E, respectively) was plotted against E, a pair of straight lines with reciprocal slopes of $+125$ and -106 mV was obtained (pH$_c$=3.68). The summit current was maximum at

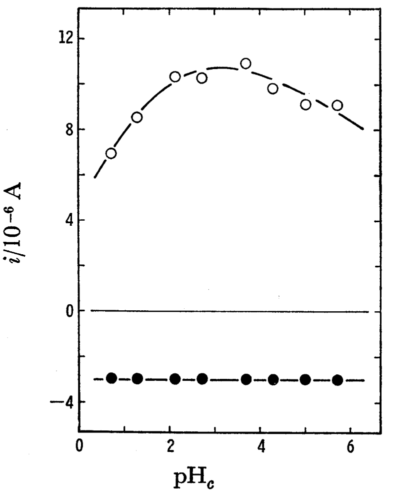


Fig. 3. pH$_c$-Dependence of i_d and i_s. 1 mmol dm^{-3} [Ru(Hedta)(H$_2$O)]; buffer solution; ionic strength= 0.2 mol dm^{-3}; ●: i_d; ○: i_s, ΔV=10 mV, f=35 Hz.

pH$_c$ values between 3 and 4, decreasing at higher and lower pH$_c$ (Fig. 3). The dependence of i_s on the frequency of the superimposed alternating voltage was examined at pH$_c$=0.72, 3.68, and 5.78 in the frequency range of 35—190 Hz, and i_s was found to be proportional to the square root of the frequency at pH$_c$= 3.68; in the other cases, the relation between i_s and the frequency was not linear.

Controlled-Potential Electrolysis. When the complex was partially reduced at the potential of the diffusion current plateau of the first step (−0.40 V), a redox polarographic step appeared at about −0.2 V. It was also noted that the reduced form of the complex was oxidized to the original form of the complex by passing air into the solution. The solution became slightly greenish when the electrolysis proceeded.

In the absence of perchlorate ions, the polarographic oxidation and reduction diffusion currents, i_d^a and i_d^c, recorded by suspending the electrolysis were plotted against the quantity of electricity consumed (Q) (Fig. 4). The reduction diffusion current decreased in proportion to the advancement of the electrolysis. The slope obtained from the decrease in $|i_d^c|$ indicated that the reduction is a one-electron process. On the contraty, i_d^a remained small during the electrolysis instead of increasing proportionally. When the partially electrolyzed solution was allowed to stand, i_d^a decreased with a half-decay time of about 30 min while i_d^c remained constant.

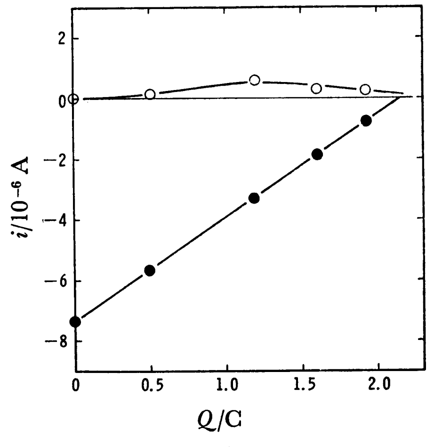


Fig. 4. Polarographic diffusion current against quantity of electricity consumed. Solution volume, 10 cm^3; 2.26 mmol dm^{-3} [Ru(Hedta)(H$_2$O)]; formate buffer; pH$_c$=4.34; ionic strength=0.5 mol dm^{-3}; 25 °C; ○: i_d^a, ●: i_d^c.

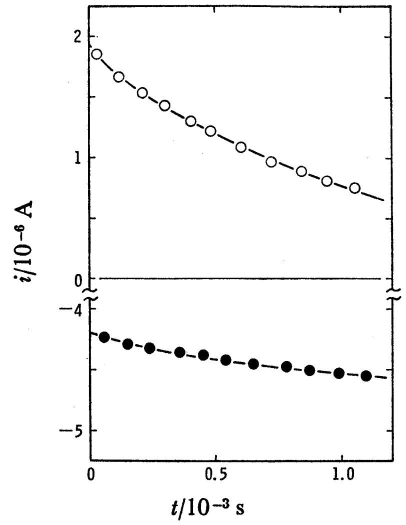
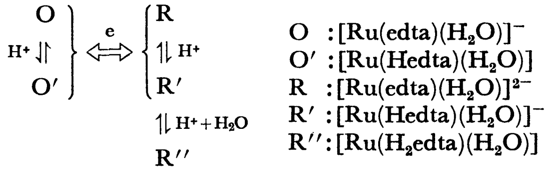


Fig. 5. Time-dependence of i_d^a and i_d^c. Formate buffer; 0.15 mol dm^{-3} NaClO$_4$; pH$_c$=4.35; ionic strength= 0.5 mol dm^{-3}; 25 °C; ○: i_d^a, ●: i_d^c.

In the solution containing perchlorate ions, the dependence of i_d^c on Q was not linear. When the electrolysis was suspended, i_d^a decreased faster than in the absence of perchlorate ions while $|i_d^c|$ increased (Fig. 5).

Discussion

Electrode Processes and Equilibria. In acid buffer solutions the first reduction step is DC-polarographically reversible, and its $E_{1/2}$ is independent of the concentration of edta^{4-} in the solution. On the basis of these observations the pH-dependence of $E_{1/2}$ can be explained in terms of a set of acid-base equilibria (Fig. 6).



O : [Ru(edta)(H$_2$O)]$^-$
O′ : [Ru(Hedta)(H$_2$O)]
R : [Ru(edta)(H$_2$O)]$^{2-}$
R′ : [Ru(Hedta)(H$_2$O)]$^-$
R″: [Ru(H$_2$edta)(H$_2$O)]

Fig. 6. Electrode process and acid-base equilibria.

Here [Ru(edta)(OH)]$^{2-}$ is ignored, because its concentration is negligible in acid solutions. Furthermore, any protonated species of the Ru(III) complex can be excluded by the fact that the electronic spectra of the complex in acid solutions were unchanged up to pH$_c$= 1. If each reaction is virtually in equilibrium in the course of the DC-polarographic reduction, the current-potential curve should follow Eqs. (1a) and (1b).

$$E = E_{1/2} - \frac{RT}{F} \ln \frac{i}{i_d - i} \tag{1a}$$

with

$$E_{1/2} = E_c + \frac{RT}{F} \ln \frac{([\mathrm{H^+}]/c^{\ominus})^2 + K_R[\mathrm{H^+}]/c^{\ominus} + K_R K_R'}{([\mathrm{H^+}]/c^{\ominus}) + K_0} \tag{1b}$$

where

$$K_0 = [\mathrm{O}][\mathrm{H^+}]/[\mathrm{O'}]c^{\ominus}$$

$$K_R = [\mathrm{R}][\mathrm{H^+}]/[\mathrm{R'}]c^{\ominus}$$

$$K_R' = [\mathrm{R'}][\mathrm{H^+}]/[\mathrm{R''}]c^{\ominus} \text{ with } c^{\ominus} = 1 \text{ mol dm}^{-3}.$$

Among these constants $K_0 = 4.29 \times 10^{-3}$ was determined by the titration of [Ru(Hedta)(H_2O)]. The others were calculated by applying the method of least squares to Eq. (1b). The best fit was obtained by the following set: $E_c = -0.078$ V, $K_R = 6.20 \times 10^{-4}$, and $K_R' = 2.53 \times 10^{-2}$. The agreement between the 'best' curve and the experimental data is excellent (Fig. 2).

The points in Fig. 2 lying along a single curve were obtained by using different buffer solutions. It follows that no anion is involved in the proton uptake of the reduced form. Although no direct evidence has yet been obtained for the protonated reduced form, the value of K_R' seems reasonable.

Polarographic Reversibility. The result of coulometry shows that the charge number of the reduction step is one. The log-plot of the DC step and the single redox step observed in the partially electrolyzed solutions show that the first step is reversible at $\mathrm{pH}_c < 5$.

The AC reversibility was tested by analyzing the shape and height of the AC wave and the frequency dependence. The AC log-plot resulted in a pair of straight lines whose reciprocal slopes were in fair agreement with the reversible value of ± 118 mV.[26] For an AC-reversible wave the ratio of the summit AC current (i_s) to the diffusion current (i_d) is given by Eq. (2).

$$\frac{i_s}{i_d} = \frac{nF\Delta V(2\pi f)^{1/2}}{4RT(7/3\pi)^{1/2} t_d^{-1/2}(1+x)} \tag{2}$$

with

$$x = bD^{1/2} m^{1/3} t_d^{1/6}$$

Where ΔV and f are the amplitude and frequency of the superimposed AC voltage and t_d is the mean drop time in the potential region where i_s and i_d are measured; the constant b is 39.7 $\mathrm{m^{-1}\,kg^{1/3}}$ given by Koutecký.[22] Inserting the necessary values into Eq. (2) one obtains $i_s/i_d = 3.34$. The corresponding experimental value at $\mathrm{pH}_c = 3.68$ was 3.11; the agreement is reasonable. The summit current was proportional to $f^{1/2}$ up to $f = 190$ Hz as expected for a reversible case. All these data demonstrate that at $\mathrm{pH}_c = 3$—5 the reduction process is reversible in both AC- and DC-polarographic senses.

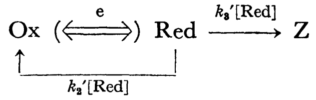
However, at $\mathrm{pH}_c > 5$ both AC and DC polarograms became more or less irreversible. This seems to suggest that the reduction of $[\mathrm{Ru(edta)(OH)}]^{2-}$ is less reversible. At $\mathrm{pH}_c < 2$, on the other hand, the DC step remained reversible, but the AC wave broadened and its height decreased. A study on the AC wave using a phase-selective AC polarograph indicated a reversible electron-transfer followed by a relatively slow chemical reaction.[27] The less reversible behavior of the AC wave may be explained by assuming that the proton dissociation of the reduced form, which involves the substitution of one of the ligating water molecules by the carboxyl group, is sluggish compared with the frequency of the superimposed AC voltage.

Chemical Reactions Subsequent to Electrode Reaction. As mentioned earlier, the reduction of the complex proceeds through a one-electron process. But the polarograms recorded in the course of the electrolysis showed an unusual behavior of the reduced form of the complex. The gradual decrease in i_d^a observed in the absence of perchlorate ions, when the partially electrolyzed solution was allowed to stand, shows the existence of at least one following chemical reaction by which the reduced form is consumed. We call this chemical reaction the deactivation reaction since the product is polarographically inactive as demonstrated by the fact that no polarographic step was observed when the solution was left to stand for a sufficient time after the completion of the electrolysis.

In the presence of perchlorate ions not only did i_d^a decrease but $|i_d^c|$ increased (Fig. 5). The faster decrease in i_d^a than that observed in the absence of perchlorate ions indicates the contribution of another chemical reaction in which the reduced form and perchlorate ions react. The increase in $|i_d^c|$ indicates the regeneration of the original form of the complex. These facts suggest that perchlorate ions reoxidize the reduced form to the original oxidized form. We call this reaction the reoxidation reaction. In the presence of perchlorate ions, the deactivation and reoxidation reactions occur simultaneously.

Kinetic Study of Chemical Reactions. The rate constants of both reactions can be determined by analyzing the time-dependence of i_d^a and i_d^c when the electrolysis is suspended.

The following reaction scheme is proposed:



$$\begin{tikzcd} \mathrm{Ox} \arrow[r, shift left, "e"] & \mathrm{Red} \arrow[l, shift left] \arrow[r, "k_3'\mathrm{[Red]}"] \arrow[l, bend left, "k_2'\mathrm{[Red]}"] & \mathrm{Z} \end{tikzcd}$$

where Ox, Red, and Z represent the oxidized (equilibrium mixture of O and O′), reduced (equilibrium mixture of R, R′, and R″), and deactivated forms of the complex, respectively, and [Red] is the concentration of Red. If the rate of decrease of [Red] is assumed to be first-order with respect to [Red], the time differentiation of [Red], when the electrolysis is suspended, is given by:

$$-\frac{\mathrm{d[Red]}}{\mathrm{d}t} = (k_2' + k_3')[\mathrm{Red}] \tag{3}$$

where k_2' and k_3' are the apparent first-order rate constants for the respective reactions. Integrating Eq. (3) with the boundary condition, $[\mathrm{Red}] = [\mathrm{Red}]_0$ at $t = 0$, one obtains:

$$[\mathrm{Red}] = [\mathrm{Red}]_0 \exp\{-(k_2' + k_3')t\}. \tag{4}$$

Similarly, the time differentiation of the concentration of Ox under the same conditions is

$$\frac{\mathrm{d[Ox]}}{\mathrm{d}t} = k_2'[\mathrm{Red}]. \tag{5}$$

The equation obtained by inserting Eq. (4) into Eq. (5) is integrated with the boundary condition, [Ox]=[Ox]$_0$ at t=0. Rearranging the resulting expression, we have

$$\frac{k_3}{k_2'+k_3'} = \frac{[\mathrm{Ox}]-[\mathrm{Ox}]_0}{[\mathrm{Red}]-[\mathrm{Red}]_0}. \tag{6}$$

By assuming equal diffusion coefficients for both Red and Ox, Eqs. (4) and (6) are expressed as follows:

$$\ln (i_\mathrm{d}{}^\mathrm{a}/i_\mathrm{d,0}^\mathrm{a}) = -(k_2'+k_3')t \tag{7}$$

$$\frac{i_\mathrm{d}{}^\mathrm{c}-i_\mathrm{d,0}^\mathrm{c}}{i_\mathrm{d,0}^\mathrm{a}-i_\mathrm{d}{}^\mathrm{a}} = \frac{k_2'}{k_2'+k_3'} \tag{8}$$

where $i_\mathrm{b,o}^\mathrm{a}$ and $i_\mathrm{b,o}^\mathrm{a}$ are the respective diffusion currents at t=0.

TABLE 1. KINETIC DATA FOR REOXIDATION AND DEACTIVATION RATES

No.	$\frac{[\mathrm{H}^+]}{10^{-4}\mathrm{M}}$	$\frac{[\mathrm{ClO_4}^-]}{\mathrm{M}}$	$\frac{[\mathrm{NaCl}]}{\mathrm{M}}$	$\frac{k_2'}{10^{-4}\,\mathrm{s}^{-1}}$	$\frac{k_3'}{10^{-4}\,\mathrm{s}^{-1}}$
1	3.39	0	0.30		19.1
2	2.19	0	0.25		15.6
3	0.457	0	0.15		7.00
4	1.17	0	0.195		11.1
5	0.457	0.15	0	2.66	6.28
6	0.437	0.15	0	2.71	6.25
7	3.24	0.15	0.05	1.79	19.0
8	0.457	0.10	0.05	1.54	6.06
9	0.457	0	0.15		6.24
10	0.457	0.15	0	2.37	5.97
11	0.457	0.04	0.11	0.50	6.57
12	0.457	0.05	0.10	0.57	6.52
13	1.41	0.15	0.045	2.23	10.9
14	3.16	0.15	0.10	2.75	17.3
15	2.75	0.15	0.10	2.97	15.8
16	0.59	0	0.15		6.33[a]
17	3.63	0	0.30		18.7
18	3.63	0	0.30		18.3[a]
19	1.05	0	0.195		11.7
20	1.05	0	0.195		11.8
21	1.05	0.15	0.045	2.54	12.0
22	1.05	0	0.195		19.7 (30.0 °C)
23	1.05	0.15	0.045	5.25	20.7 (30.0 °C)
24	1.05	0	0.195		4.15(10.0 °C)
25	1.05	0.15	0.045	0.36	4.54(10.0 °C)
26	1.05	0	0.195		5.39(15.0 °C)
27	1.05	0.15	0.045	0.645	5.06(15.0 °C)
28	1.05	0	0.195		7.60(20.0 °C)
29	1.05	0.15	0.045	1.27	8.35(20.0 °C)

M represents mol cm^{-3}. a) The solution contains 0.1 mol dm^{-3} H$_4$edta.

Equations (7) and (8) were experimentally satisfied, and by solving them k_2' and k_3' were obtained as shown in Table 1. k_3' was found to be independent of perchlorate ion concentration. It seems that the deactivation process involves a reaction between Ru(II)edta species and formic acid similar to that reported in the case of the tetrachlororuthenate(II)-formic acid system.[28] Details on the kinetics of this reaction and identification of the reaction product will be reported separately.

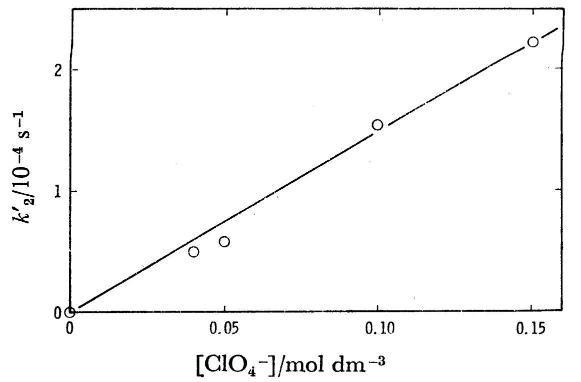


Fig. 7. Effect of perchlorate ion concentration on reoxidation rate. Formate buffer; ionic strength=0.5 mol dm^{-3}; 25 °C.

The apparent rate constant of the reoxidation, k_2', was independent of the hydrogen ion concentration and formic acid concentration. When k_2' was plotted against perchlorate ion concentration a straight line was obtained (Fig. 7), from which the rate constant for the reoxidation, k_2 at 25.0 °C is estimated at the 90% confidence limit as follows:

$$k_2 = \frac{k_2'}{[\mathrm{ClO_4}^-]} = (1.38\pm0.26)\times10^{-3}\,\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{s}^{-1}$$

Linear Arrhenius plots are obtained for k_2. The activation parameters for the reoxidation process are calculated at the 90% confidence limit by applying the rate theory of Eyring with the assumption tnat the transmission coefficient and quotient of activity coefficients are unity. At 25.0 °C, $\Delta H^{\ast}$ and $\Delta S^{\ast}$ obtained are as follows:

$$\Delta H^{\ast} = (9.41\pm17.6)\times10^3\,\mathrm{J\ mol}^{-1},$$

$$\Delta S^{\ast} = (19.0\pm6.3)\,\mathrm{J\ K}^{-1}\,\mathrm{mol}^{-1}.$$

The value of $\Delta H^{\ast}$, which is very similar to those for other ruthenium(II) substitution reactions[13–15] but much larger than those for ruthenium(II)—ruthenium(III) electron transfer reactions,[11] seems to indicate that the rate determining step of the reoxidation reaction is the substitution of perchlorate ion on the reduced form of the complex. The most probable mechanism for the attack of perchlorate ion on the reduced form is similar to that proposed by Taube[9] in the case of hexaammineruthenium(II) ions.

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