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Reaction of Ru(II)-EDTA in Sodium Formate–Formic Acid Solutions*

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When $[Ru^{III}(Hedta)(H_2O)]$ was reduced at mercury electrode in sodium formate–formic acid solutions, the reduced species gradually became polarographically inactive. The final product of the deactivation reaction was isolated and identified as $Na_2[Ru^{II}(edta)(CO)]$. The kinetics follows the second-order rate equation, $-dc_1/dt=k_{obsd}\,c_1\,c_2$, where $c_1=[[Ru^{II}(Hedta)(H_2O)]^-]+[[Ru^{II}(edta)(H_2O)]^{2-}]$ and $c_2=[HCOO^-]+[HCOOH]$. The k_{obsd} value was found to be expressed by $k\,[H^+]/(K_A+[H^+])(K_R+[H^+])$, where $K_A(=3.28\times10^{-4}\ mol\ dm^{-3})$ and $K_R(=6.92\times10^{-4}\ mol\ dm^{-3})$ are the acid-dissociation constants of formic acid and $[Ru^{II}(Hedta)(H_2O)]^-$, respectively, with $k=1.01\times10^{-5}\ s^{-1}$ at 25 °C (ionic strength$=0.5\ mol\ dm^{-3}$). Several possible mechanisms for the reaction were discussed. Probably the reaction proceeds through the formation of an intermediate involving one formate anion followed by dehydration and rearrangement.

Formation of carbonyls through decarbonylation of organic compounds by metal complexes has attracted considerable interest in recent years and a number of such reactions have been reported.[1–8] Halpern and Kemp studied the decarbonylation of formic acid by ruthenium(II) chloride in strongly acid solutions (about 3 mol dm^{-3} HCl) and obtained $(NH_4)[Ru^{II}(CO)Cl_4(H_2O)]$.[3] They also examined the kinetics of the decarbonylation and claimed that the reaction is of the second-order with respect to the ruthenium(II) species and *formic acid.* However, their results may be equally well explained by postulating formate anion as a reactant.

It has been pointed out[9] that electrolytically generated $[Ru^{II}(Hedta)(H_2O)]^-$ or $[Ru^{II}(edta)(H_2O)]^{2-}$ ** undergoes a deactivation process in formate–formic acid buffer solutions.

In the present work the final reaction product of this process has been identified as a carbonyl–edta-complex of ruthenium(II), the kinetics of its formation being examined in detail.

Experimental

Materials. Aqua(hydrogenethylenediaminetetraacetato)ruthenium(III) tetrahydrate, $[Ru(Hedta)(H_2O)]\cdot4H_2O$, was prepared according to the procedure of Mukaida *et al.*[10] with some modifications. An intensely blue ruthenium(II) cluster complex[11] was prepared by evaporating a mixture of 200 cm^3 of ethanol and 150 cm^3 of 3 mol dm^{-3} HCl solution containing 1.05 g of ruthenium(III) on a water bath. It was dissolved in a small portion of water, and a solution of 2.4 g of disodium ethylenediaminetetraacetate was added. The mixture, after being acidified by the addition of 1 cm^3 of concentrated hydrochloric acid, was evaporated nearly to dryness. The residue was dissolved in a small amount of water and evaporated again. The procedure was repeated several times until an orange solution was obtained on dissolving the residue. The pH of solution was then adjusted to *ca.* 2 with a sodium hydroxide solution. Ethanol was solwly added to the solution with stirring until a yellow precipitate appeared, and the mixture was left to stand overnight in a refrigerator. The yellow precipitate was filtered, washed several times with ethanol, and then dried *in vacuo* at 40 °C (yield, 2.4 g). Found: Ru, 20.57; C, 24.61; N, 5.60; H, 4.48%. Calcd for $[Ru(Hedta)(H_2O)]\cdot4H_2O$: Ru, 21.04; C, 25.00; N, 5.83; H, 4.28%. The IR spectrum of the product agreed with that reported by Mukaida *et al.* Its purity as determined by alkalimetric titration was 99.3%.

Deionized water distilled in an all-glass apparatus was used for the electrochemical experiments. The oxygen dissolved in the electrolytic solutions was removed by bubbling nitrogen gas which had been passed through acid vanadium(II) sulfate solution and then distilled water. The other chemicals used were of guaranteed reagent grade.

Measurements. All the electrochemical measurements were carried out at (25.0±0.1) °C under nitrogen atmosphere. All the potentials were measured against a saturated calomel electrode (SCE).

The electrolysis for the preparation of the final reaction product was performed with a Yanagimoto Controlled Potential Electrolyzer CE-3. The geometry of the electrolytic cell is illustrated in Fig. 1.

Controlled potential coulometry was carried out as described earlier[9] except that the integration of the electrolytic current was carried out on a digital counter (Takedariken, Universal Counter TR-5104) by converting the current signal into pulses with a voltage-frequency converter (Aiko VF 500).[12]

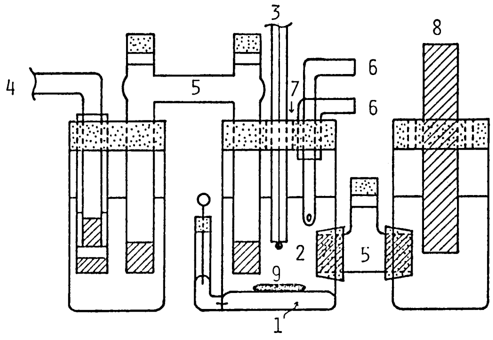

Fig. 1. Electrolytic cell for recorvery of the final reaction product.

1. Mercury pool working electrode (*ca.* 7.2 cm^2); 2. electrolytic solution; 3. DME; 4. to SCE; 5. salt bridge (1 mol dm^{-3} sodium formate) with filter paper plugs; 6. gas inlets; 7. gas outlet; 8. carbon anode immersed in 1 mol dm^{-3} sodium formate solution; 9. magnetic stirrer.

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** The following abbreviations will be used: Ru(II)-Hedta$^-$ for $[Ru^{II}(Hedta)(H_2O)]^-$, Ru(III)-Hedta for $[Ru^{III}(Hedta)(H_2O)]$, Ru(II)-edta^{2-} for $[Ru^{II}(edta)(H_2O)]^{2-}$, and Ru(III)-edta$^-$ for $[Ru^{III}(edta)(H_2O)]^-$.

All the polarograms were recorded with a potentiostat-type dc-ac polarograph constructed in this laboratory. The drop time of the DME was controlled by an electronic drop-dislodger.[13,14] The device incorporated a relay which cuts off the polarographic current signal to the recorder at the moment of drop dislodging in order to suppress the noise accompanying the drop fall and to enhance the S/N ratio.[15] The polarographic current signal was sampled at 3.50 s after dislodgement. The flow rate of mercury from the DME was 1.78 mg $\mathrm{s^{-1}}$ under a mercury head of 50 cm. All the polarographic currents were corrected for the residual currents.

Infrared spectra were recorded with a Hitachi EPI-G2 IR spectrophotometer by the potassium bromide disk technique. Visible spectra were measured with a Hitachi 124 spectrophotometer. Conductivity was measured in distilled water with a TOA Electronics Conduct Meter CM-6A. Magnetic properties were measured by the Gouy method.

All the $\mathrm{pH_c}$[†] values of the solutions were determined with a Radiometer pH meter 25E equipped with a glass electrode Type G202B and an SCE Type K401, whose meter readings were calibrated against standard hydrochloric acid solutions adjusted to 0.5 mol $\mathrm{dm^{-3}}$ of ionic strength by the addition of NaCl.

Analysis. Elemental analysis of C, H, and N was carried out by means of a Yanagimoto MT2 CHN Corder.

Spectrophotometric determination of ruthenium in the complexes was carried out according to the ruthenate method.[16] A weighed sample (*ca.* 10 mg) was decomposed in a nickel crucible by heating, and then fused with 0.1 g of potassium hydroxide and 0.3 g of potassium nitrate. The melt was dissolved in 50 $\mathrm{cm^3}$ of a solution containing 10 g of potassium hydroxide, the solution volume then being adjusted to 100 $\mathrm{cm^3}$ with water. The absorbance of the solution was measured at 465 nm.

The content of sodium ions in the final reaction product was determined by the cation-exchange method. A weighed sample (*ca.* 0.1 g) dissolved in 10 $\mathrm{cm^3}$ of water was passed through a column of an H-form cation exchanger (Dowex 50-X8, 100—200 mesh), the column was washed with water and the combined eluate was titrated with a standard sodium hydroxide solution.

The content of water of crystallization was estimated by thermal gravimetric analysis with a Rigakudenki TG-DTA M8075.

Procedure. *Isolation of the Final Reaction Product*: A 20 $\mathrm{cm^3}$ portion of sodium formate–formic acid (0.5 mol $\mathrm{dm^{-3}}$ each) containing 1.0 g of Ru(III)-Hedta was placed in the electrolytic cell and deoxygenated. Electrolysis was carried out at −0.5 V with stirring until more than 99% of the Ru(III)-Hedta was reduced. After the cell solution had been left to stand for 2 h under a nitrogen atmosphere, it was transferred into a flask and concentrated to one-fourth the initial volume under a reduced pressure at 40 °C. Ethanol was slowly added to the resulting solution until fine, pale yellow crystals precipitated; the mixture was allowed to stand in a refrigerator overnight. The precipitate, after being filtered, was recrystallized from methanol. The product was washed several times with ethanol and then dried *in vacuo* at 40 °C.

Measurement of Acid-dissociation Constants: The acid-dissociation constants of formic acid and Ru(III)-Hedta in 0.5 mol $\mathrm{dm^{-3}}$ NaCl solution were determined from the respective pH-titration curves.[17] The constnat of Ru(II)-Hedta$^-$ was calculated from the $\mathrm{pH_c}$ dependence of the reversible half-wave potential of the Ru(III)-Hedta reduction step in acid buffer solutions (sodium chloride–hydrochloric acid–0.001% Triton X-100 for $\mathrm{pH_c}<2$, sodium formate–formic acid for $2<\mathrm{pH_c}<4$, sodium acetate–acetic acid for $\mathrm{pH_c}>4$; ionic strength=0.5 mol $\mathrm{dm^{-3}}$ (NaCl)). The method was essentially the same as that described earlier;[9] but in the present case the data for $\mathrm{pH_c}=1.8$—5.5 were used so as to secure a higher precision for K_R. The values are given in Table 1.

Table 1. Acid-dissociation constants
(Ionic strength=0.5 mol $\mathrm{dm^{-3}}$, 25 °C), $K=[\mathrm{H^+}][\mathrm{X}]/[\mathrm{HX}]$.

Symbol	X	K/mol $\mathrm{dm^{-3}}$
K_A	$\mathrm{HCOO^-}$	3.28×10^{-4}
K_O	$[\mathrm{Ru^{III}(edta)(H_2O)}]^-$	2.22×10^{-3}
K_R	$[\mathrm{Ru^{II}(edta)(H_2O)}]^{2-}$	6.92×10^{-4}

Kinetic Measurements: For the kinetic measurements, sodium formate was used as the supporting electrolyte and the ionic strength of the solution was adjusted to 0.5 mol $\mathrm{dm^{-3}}$ by the addition of sodium *p*-toluenesulfonate. A 12 $\mathrm{cm^3}$ portion of the supporting electrolyte solution was placed in the cell and deoxygenated. The solution was pre-electrolyzed at −0.5 V unitl a constant electrolytic current (usually about 3 μA) was reached. A known amount of Ru(III)-Hedta (*ca.* 20 μmol) was dissolved in the pre-electrolyzed solution, and the polarogram was recorded. When *ca.* 80% of Ru(III)-Hedta was reduced at −0.5 V to the bivalent state, a known amount of concentrated formic acid was injected into the solution from a microsyringe. After bubbling the nitrogen for 2—3 min, the decreasing anodic diffusion current at 0 V was recorded (chart speed, 2.5×10^{-2} cm $\mathrm{s^{-1}}$) until it reached one-tenth the initial current.

Results and Discussion

Final Reaction Product. Elemental analyses of the final reaction product gave Ru, 19.48; C, 26.09; N, 5.59; H, 3.30%. The thermal gravimetric analysis showed that the water content in the product is 6.5%. These results indicate that the product contains 11 carbon, 2 nitrogen and 16—17 hydrogen atoms, and 2 molecules of water per ruthenium atom. The presence of protonated carboxyl groups and coordinated water is excluded by the fact that the final reaction product had no dissociable hydrogen. The cation-exchange experiment showed the complex ion in the product to be an anion, the number of sodium ions per ruthenium atom being 1.92.

The IR spectrum of the product is similar to that of the Ru(III)-Hedta. Two points, the presence of a very strong absorption at 1940 $\mathrm{cm^{-1}}$ and the absence of the $\rangle$C=O stretching band which would be expected for a protonated carboxyl group (1730 $\mathrm{cm^{-1}}$ for Ru(III)-Hedta), were noted. The former strongly suggests the existence of a carbonyl group coordinated to ruthenium (II).[2,3,18] The latter indicates that each of the four carboxyl groups is either ionized or coordinated; in this event the $\rangle$C=O absorption band should appear at 1590—1650 $\mathrm{cm^{-1}}$.[19] In fact, a band was observed at 1630 $\mathrm{cm^{-1}}$.

The oxidation state of the ruthenium in the final reaction product is considered to be II (t_{2g}^6) since the substance is diamagnetic. This view is supported by the fact that the product in acetate–acetic acid buffer solutions shows no polarographic step in the potential

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

range +0.2—−1.2 V. The effect of the coordinating carbonyl in ruthenium(II) complexes has been discussed in terms of the strong back-bonding with the metal orbitals of d_π-symmetry.[20] Coordination of carbonyl to ruthenium(II) renders the complex much less oxidizable. The frequency of the CO band also leads to the same conclusion: if the oxidation state of ruthenium were higher than II, the frequency would be higher because of the increase in positive charge on the central atom; for example, the ν(CO) is 1950 cm^{-1} in $(NH_4)_2[Ru^{II}Cl_4(CO)(H_2O)]$ and 2059 cm^{-1} in $(NH_4)_2[Ru^{III}Cl_5(CO)]$.[2] We infer $Na_2[Ru^{II}(edta)(CO)]\cdot 2H_2O$ as the formula of the final reaction product. The elemental composition calculated on the basis of the formula is in line with the experimental values: Ru, 20.24; C, 26.46; N, 5.61; H, 3.23%.

The molar conductivity of the product at 8.01×10^{-4} mol dm^{-3} in aqueous solution was 250 S mol^{-1} cm^2 at 25 °C, which is reasonable for a 1 : 2 type electrolyte.

The absorption peak in the visible region was at 428 nm at which the molar absorption coefficent was 9.06×10^4 mol^{-1} cm^2.

Results of Kinetic Studies. When Ru(III)-Hedta was partially electrolyzed in solutions containing sodium formate and sodium *p*-toluenesulfonate at a potential on the diffusion-current plateau of its reduction step, a single oxidation-reduction polarographic step appeared at about −0.25 V. The anodic limiting current, I_a, was proved to be diffusion-controlled, being proportional to the quantity of electricity consumed for the reduction, *i.e.*, to the total concentration of the Ru(II) species (in such weakly alkaline solutions, $[Ru^{II}(edta)(OH)]^{3-}$ is also present together with Ru(II)-edta^{2-}). No change in the polarogram was observed at least for a few hours at 25 °C.

When formic acid was present, however, the anodic current decreased with time as shown in Fig. 2, while the cathodic current remained constant. In the presence of excess formic acid–formate ion (at least 50-fold the concentration of Ru(II) species), the rate of decrease of the anodic diffusion current always obeyed the pseudo-first-order rate expression (Eq. 1) until the reaction had proceeded at least 80% to completion (Fig. 3):

$$-\ln\frac{I_a(t)}{I_a(0)} = k'_{\text{obsd}}\,t, \tag{1}$$

where $I_a(t)$ and $I_a(0)$ are the anodic diffusion current at time t and $t=0$, respectively. The values of k'_{obsd} determined from the slopes of the first-order rate plots were substantially independent of the concentrations of initially present ruthenium(II) and coexisting ruthenium(III) species.

At a given hydrogen ion concentration, k'_{obsd} was proportional to the sum of the concentrations of formate ion and formic acid (Fig. 4). Hence Eq. 1 becomes

$$-\ln\frac{I_a(t)}{I_a(0)} = k_{\text{obsd}}\,c_2\,t, \tag{2}$$

where $c_2=[HCOO^-]+[HCOOH]$ and k_{obsd} is the second-order rate constant. As seen from Fig. 5, k_{obsd} is a function of the hydrogen ion concentration, increasing almost linearly up to a maximum at $[H^+]=5\times10^{-4}$ mol dm^{-3}, after which it decreased slowly. The kinetic data are summarized in Table 2.

Interpretation of Kinetic Results. Under the experimental conditions there may be four reactant species participating in the deactivation reaction: Ru(II)-Hedta$^-$, Ru(II)-edta^{2-}, HCOO$^-$, and HCOOH. Here, $[Ru^{II}(edta)(OH)]^{3-}$ is ignored because the acid-dissociation constant for

$$[Ru^{II}(edta)(H_2O)]^{2-} \rightleftharpoons [Ru^{II}(edta)(OH)]^{3-} + H^+$$

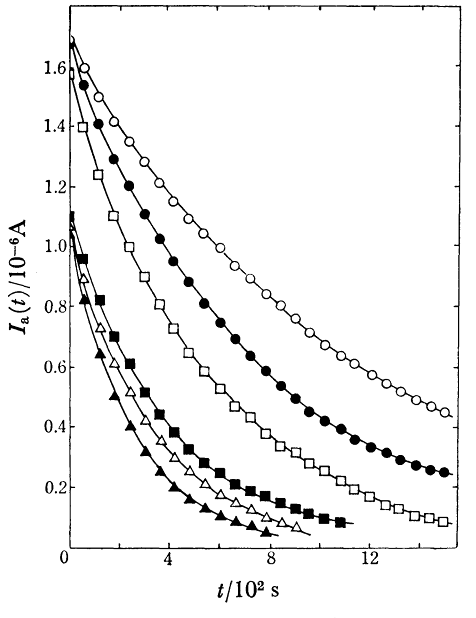

Fig. 2. Typical decay curves (ionic strength=0.5 mol dm^{-3}, 25 °C) with reference to Table 2.
○, No. 10; ●, No. 11; □, No. 9; ■, No. 14; △, No. 12; ▲ No. 13.

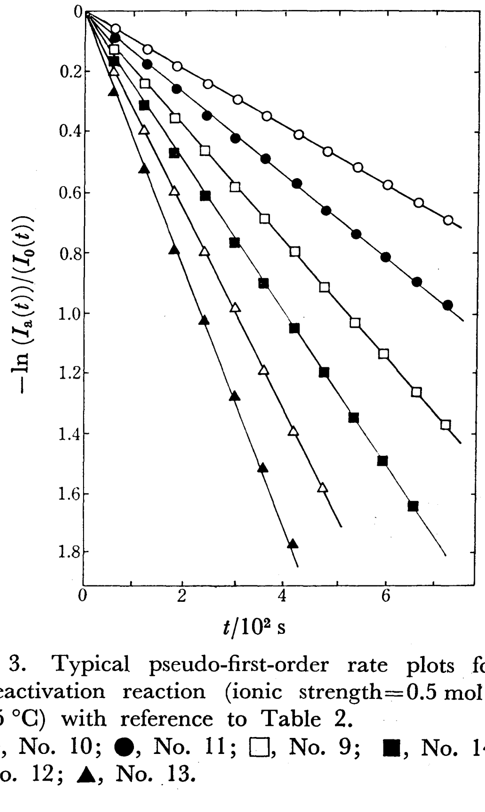

Fig. 3. Typical pseudo-first-order rate plots for the deactivation reaction (ionic strength=0.5 mol dm^{-3}, 25 °C) with reference to Table 2.
○, No. 10; ●, No. 11; □, No. 9; ■, No. 14; △, No. 12; ▲, No. 13.

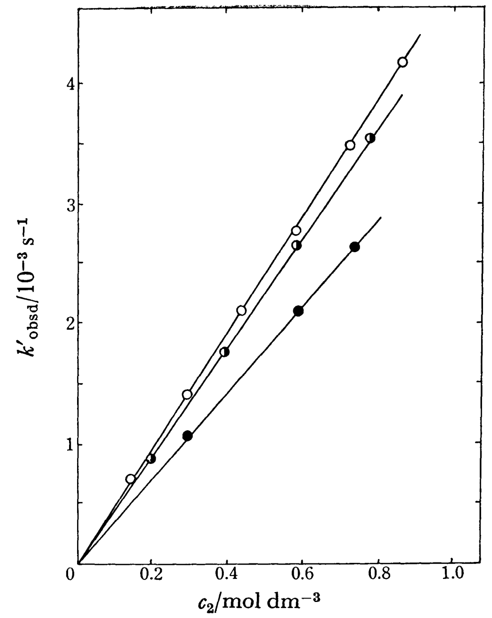

Fig. 4. Dependence of k'_{obsd} on c_2 at given hydrogen concentrations (ionic strength=0.5 mol dm^{-3}, 25 °C) with reference to Table 2.
$c_2=[HCOO^-]+[HCOOH]$; ○, No. 18—23; ◑, No. 9—14; ●, No. 3—5.

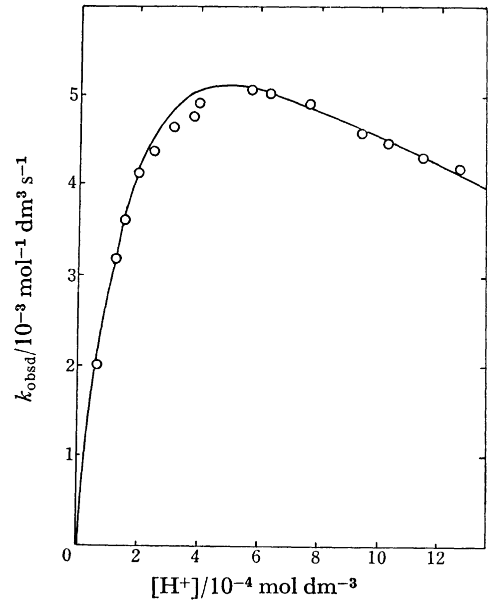

Fig. 5. Dependence of k_{obsd} on hydrogen ion concentration (ionic strength=0.5 mol dm^{-3}, 25 °C). The curve is calculated from Eq. 8 with $k=1.01\times10^{-5}\,s^{-1}$.

should be appreciably smaller than that of the corresponding Ru(III)-edta$^-$ (pK=7.63)[9] so that its concentration is negligible in formic acid–formate buffer solutions.

There are several mechanisms involving these four reactants that can explain the experimental data. Most probably, the reaction will proceed through some intermediate(s) which contains formate ion or formic acid:

$$\text{Reactants} \xrightarrow{\text{(I)}} \text{Intermediate(s)} \xrightarrow{\text{(II)}} \text{Product}$$

Either step (I) or step (II) may be rate-determining.
Case I: step (I) rate-determining.

TABLE 2. KINETIC DATA FOR DEACTIVATION RATE (ionic strength=0.5 mol dm^{-3}, 25 °C)

No.	$[H^+]$ / 10^{-4} mol dm^{-3}	c_2 / mol dm^{-3}	k'_{obsd} / 10^{-3} s^{-1}	k_{obsd} / 10^{-3} mol^{-1} dm^3 s^{-1}
1	0.164	0.596	1.20	2.01
2	1.26	0.347	1.10	3.17
3	1.51	0.297	1.06	3.57
4	1.55	0.591	2.11	3.57
5	1.55	0.737	2.63	3.57
6	2.00	0.247	1.02	4.13
7	2.44	0.442	1.92	4.34
8	2.51	0.442	1.91	4.32
9	3.09	0.392	1.80	4.59
10	3.16	0.198	0.914	4.62
11	3.16	0.295	1.36	4.61
12	3.16	0.779	3.53	4.53
13	3.16	0.970	4.35	4.48
14	3.24	0.586	2.67	4.56
15	3.86	0.178	0.835	4.69
16	3.98	0.344	1.69	4.91
17	5.62	0.313	1.58	5.05
18	6.31	0.294	1.45	4.93
19	6.46	0.148	0.708	4.78
20	6.46	0.438	2.09	4.77
21	6.61	0.582	2.77	4.76
22	6.61	0.725	3.48	4.80
23	6.66	0.866	4.17	4.82
24	7.64	0.273	1.36	4.98
25	9.33	0.263	1.21	4.60
26	10.3	0.256	1.15	4.49
27	11.4	0.251	1.09	4.34
28	12.7	0.244	1.05	4.30

$c_2=[HCOO^-]+[HCOOH]$

Mechanism 1a

$$\text{Ru(II)-Hedta}^- + \text{HCOOH} \xrightarrow{k_1} \text{intermediate,} \qquad \text{(R1)}$$

$$\text{Ru(II)-Hedta}^- + \text{HCOO}^- \xrightarrow{k_2} \text{intermediate,} \qquad \text{(R2)}$$

$$\text{Ru(II)-edta}^{2-} + \text{HCOOH} \xrightarrow{k_3} \text{intermediate,} \qquad \text{(R3)}$$

$$\text{Ru(II)-edta}^{2-} + \text{HCOO}^- \xrightarrow{k_4} \text{intermediate,} \qquad \text{(R4)}$$

where k_1, k_2, k_3, and k_4 are the corresponding second-order rate constants. If these reactions proceed in parallel, the rate of decrease of the total concentration of the Ru(II) species (c_1=[Ru(II)-Hedta$^-$]+[Ru(II)-edta^{2-}]), is given by

$$\begin{aligned} -\frac{dc_1}{dt} = {} & k_1[\text{Ru(II)-Hedta}^-][\text{HCOOH}] \\ & + k_2[\text{Ru(II)-Hedta}^-][\text{HCOO}^-] \\ & + k_3[\text{Ru(II)-edta}^{2-}][\text{HCOOH}] \\ & + k_4[\text{Ru(II)-edta}^{2-}][\text{HCOO}^-]. \end{aligned} \qquad (3)$$

Since the proton transfer reactions between Ru(II)-Hedta$^-$ and Ru(II)-edta^{2-} and between HCOOH and HCOO$^-$ must be very fast and remain in a quasi-equilibrium state so that (R2) and (R3) are kinetically indistinguishable, the above expression is reduced to

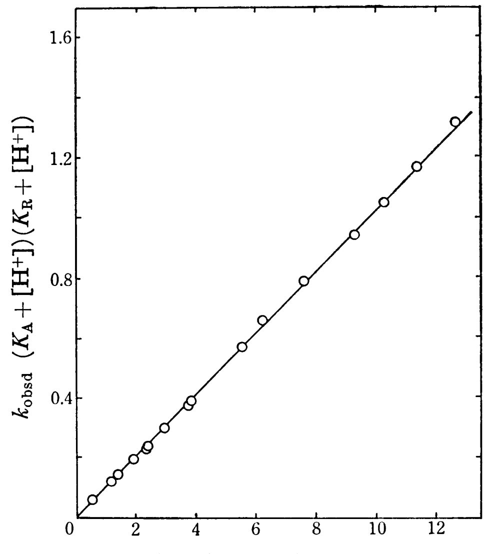

Fig. 6. Plot of k_{obsd} $(K_A+[H^+])(K_R+[H^+])$ against hydrogen ion concentration (ionic strength=0.5 mol dm^{-3}, 25 °C).

$$-\frac{dc_1}{dt}=\frac{k_1[H^+]^2+(k_2K_A+k_3K_R)[H^+]+k_4K_AK_R}{(K_A+[H^+])(K_R+[H^+])}c_1c_2. \tag{4}$$

Equation 4 is integrated with $c_1=c_2(0)$ at $t=0$ and c_2=constant. Since I_a is proportional to c_1, by comparing the resulting expression with Eq. 2, we obtain

$$k_{obsd}=\frac{k_1[H^+]^2+(k_2K_A+k_3K_R)[H^+]+k_4K_AK_R}{(K_A+[H^+])(K_R+[H^+])}. \tag{5}$$

Thus the plot of $k_{obsd}(K_A+[H^+])(K_R+[H^+])$ against hydrogen ion concentration generally should be a parabola.

The plot gives a straight line with zero intercept (Fig. 6). Hence, k_1 and k_4 must be negligibly small with respect to k_2 and/or k_3, since $[H^+]$, $K_A[H^+]$, $K_R\cdot[H^+]$, and K_AK_R are of the same order of magnitude under the experimental conditions.

Mechanism 1b

The termoleclar rate determining step,

$$\text{Ru(II)-edta}^{2-}+\text{HCOO}^-+\text{H}^+\xrightarrow{k_5}\text{intermediate}, \tag{R5}$$

is also possible but seems unlikely on statistical grounds.

Case II: step (II) is rate determining. In this case step (I) is in quasi-equilibrium state.

Mechanism 2a

$$\begin{aligned}&\text{Ru(II)-Hedta}^-+\text{HCOOH}\overset{K_6}{\rightleftharpoons}\text{intermediate(6)}\\&\text{intermediate(6)}\xrightarrow{k_6}\text{product,}\end{aligned} \tag{R6}$$

$$\begin{aligned}&\text{Ru(II)-Hedta}^-+\text{HCOO}^-\overset{K_7}{\rightleftharpoons}\text{intermediate(7)}\\&\text{intermediate(7)}\xrightarrow{k_7}\text{product,}\end{aligned} \tag{R7}$$

$$\begin{aligned}&\text{Ru(II)-edta}^{2-}+\text{HCOOH}\overset{K_8}{\rightleftharpoons}\text{intermediate(8)}\\&\text{intermediate(8)}\xrightarrow{k_8}\text{product,}\end{aligned} \tag{R8}$$

$$\begin{aligned}&\text{Ru(II)-edta}^{2-}+\text{HCOO}^-\overset{K_9}{\rightleftharpoons}\text{intermediate(9)}\\&\text{intermediate(9)}\xrightarrow{k_9}\text{product,}\end{aligned} \tag{R9}$$

where K_6, K_7, K_8, and K_9 are the equilibrium constants for respective reactions, and k_6, k_7, k_8, and k_9 are the first-order rate constants for the respective intermediate. Here, intermediates(6)—(9) are not necessarily different.

If the intermediates are also oxidized at the potential where I_a is measured and their diffusion coefficients are the same or nearly the same as that of Ru(II) species, $-dI_a(t)/dt$ is proportional to

$$-d([\text{Ru(II)-Hedta}^-]+[\text{Ru(II)-edta}^{2-}]+\sum_{i=6}[\text{intermediate}(i)])/dt.$$

If these reactions proceed in parallel, a simple calculation similar to that in the preceeding section leads to

$$k_{obsd}=\frac{k_6K_6[H^+]^2+(k_7K_7K_A+k_8K_8K_R)[H^+]+k_9K_9K_AK_R}{(K_A+[H^+])(K_R+[H^+])}. \tag{6}$$

For the same reason as in the case of Mechanism 1a, the reaction paths (R6) and (R9) are neglected.

If the intermediates are electro-inactive at the potential concerned and hence I_a is proportional to Ru(II) species only, the resulting expression becomes consistent with the experimental results only when the concentrations of the intermediates are very small. In such a case k_{obsd} is obtained by Eq. 6.

Mechanism 2b

$$\begin{aligned}&\text{Ru(II)-edta}^{2-}+\text{HCOO}^-\overset{K_{10}}{\rightleftharpoons}\text{intermediate}\\&\text{intermediate}+\text{H}^+\xrightarrow{k_{10}}\text{product}\end{aligned} \tag{R10}$$

If the intermediate is electro-active, we get

$$k_{obsd}=\frac{k_{10}K_{10}K_AK_R[H^+]}{(K_A+[H^+])(K_R+[H^+])}, \tag{7}$$

which is compatible with the experimental results.

On the other hand, if the intermediates is electro-inactive, the resulting expression is reduced to Eq. 7 only when the intermediate concentration is very small.

The probable mechanisms 1a, 1b, 2a, and 2b are kinetically indistinguishable and their discrimination requires further information.

At present, the rate constant is expressed by

$$k_{obsd}=\frac{k[H^+]}{(K_A+[H^+])(K_R+[H^+])}, \tag{8}$$

where k is a constant equal to 1.01×10^{-5} s^{-1} at 25 °C (ionic strength=0.5 mol dm^{-3}).

Conclusion

Cleare and Griffith[8] in their study of the formation of halogeno-carbonyl complexes of the platinum metals identified formato-intermediates from the formic acid-hexahalogenorhodate(2−) reactions by IR spectroscopy. Although no such intermediate was identified in the case of ruthenium, they noted "indications that the reactions proceed *via* formato- and formato-halogeno-carbonyl intermediates (the use of hydrochloric acid in the reactions appears to inhibit the formation of formato complexes)."

Most probably, the present reaction also will proceed through such formato-intermediates. The reaction path that involves Ru(II)-Hedta$^-$ and HCOOH (R1 or R6) is not compatible with the experimental results. Since HCOOH does not react with Ru(II)-Hedta$^-$, it will not react with Ru(II)-edta^{2-} because it is improbable that HCOOH, being an uncharged species, behaves in an essentially different way depending on the charge of the bulky reaction partner: (R3) and (R8) are excluded. A reaction path involving no hydrogen ion such as (R4) and (R9) has been excluded on the basis of the kinetic data.

The formato-intermediate requires one proton to undergo the subsequent dehydration process to $[\text{Ru}^{\text{II}}(\text{edta})(\text{CO})]^{2-}$. The proton is involved in the rate determining step as indicated by the kinetic data. In (R2) or (R7) the proton is supplied from Ru(II)-Hedta$^-$, the concentration of which is much larger than the free hydrogen ion concentration in the solution.

The above discussion and the kinetic analysis lead to three probable mechanisms:

Mechanism 1a

$$\text{Ru(II)-Hedta}^- + \text{HCOO}^- \xrightarrow[\text{slow}]{k_2} \text{Ru(II)-Hedta-HCOO}^{2+}$$

$$\text{Ru(II)-Hedta-HCOO}^{2-} \xrightarrow[\text{fast}]{} \text{Ru}^{\text{II}}(\text{edta})(\text{CO})^{2-} + \text{H}_2\text{O}$$

Mechanism 2a

$$\text{Ru(II)-Hedta}^- + \text{HCOO}^- \overset{K_7}{\rightleftharpoons} \text{Ru(II)-Hedta-HCOO}^{2-}$$

$$\text{Ru(II)-Hedta-HCOO}^{2-} \xrightarrow[\text{slow}]{k_7} \text{Ru}^{\text{II}}(\text{edta})(\text{CO})^{2-} + \text{H}_2\text{O}$$

Mechanism 2b

$$\text{Ru(II)-edta}^{2-} + \text{HCOO}^- \overset{K_{10}}{\rightleftharpoons} \text{Ru(II)-edta-HCOO}^{3-}$$

$$\text{Ru(II)-edta-HCOO}^{3-} + \text{H}^+ \xrightarrow[\text{slow}]{k_{10}} \text{Ru}^{\text{II}}(\text{edta})(\text{CO})^{2-} + \text{H}_2\text{O}$$

The second steps of these mechanisms involve dehydration and rearrangement of the formato ligand. Direct evidence for the formato-intermediate is yet to be sought, but information on the kinetics of acetylacetonato-ruthenium(II)–formate reactions[21] suggests that it may be formed through substitution of the aqua ligand by formate ion. At present, the experimental data available are insufficient to establish the most probable mechanism. The numerical values for the rate constants as interpreted according to the three mechanisms are given in Table 3.

Equation 8 implies that the rate is maximum when $[\text{H}^+]=(K_\text{A}K_\text{R})^{1/2}$, in this case, 4.76×10^{-4} mol dm^{-3}. It should be noted that a mild acidic condition is favorable for preparing carbonyl complexes when the reaction mechanism is similar to the present one.

Table 3. Rate constant for probable mechanisms

Mechanism	k	Experimental value
1a	k_2k_R	$k_2=3.08\times10^{-2}$ mol^{-1} dm^3 s^{-1}
2a	k_7K_7	$k_7K_7=3.08\times10^{-2}$ mol^{-1} dm^3 s^{-1}
2b	$k_{10}K_{10}K_\text{A}K_\text{R}$	$k_{10}K_{10}=44.5$ mol^{-2} dm^6 s^{-1}

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