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Color Reactions of Aqua(ethylenediaminetetraacetato)ruthenate(III) with Sulfur Compounds. Kinetic Study of Thiosulfate Anation[1)]

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New color reactions of aqua(ethylenediaminetetraacetato)ruthenate(III) with sulfur compounds such as thiols, thiourea and thiosulfate have been found and investigated. It has been established that the coloration is due to the anation of the complex with sulfur compounds. In the case of thiosulfate, the reaction is first order in either reactant and independent of $[H^+]$ in the pH range 4 to 6. The rate constant (k_{AN}) was found to be 2.94 ± 0.11 M^{-1} s^{-1} at 30 °C and $I=0.1$. For a pH$>$6, the rate decreases with increase in pH due to the formation of a hydroxo complex. In the higher pH region, the reverse reaction, $[Ru(edta)(S_2O_3)]^{3-} + OH^- \rightleftarrows [Ru(edta)(OH)]^{2-} + S_2O_3^{2-}$ takes place. From the value of the equilibrium constant (K_{eq}) for this reaction, the equilibrium constant (K_{AN}) for thiosulfate anation has been estimated as, $\log K_{AN} = 5.02$ at 30 °C and $I=0.1$.

In the course of the study on the redox reaction of ethylenediaminetetraacetatoruthenate(III),[2)] it was found that the complex solution gave an intense red color by the addition of sulfur compounds, such as cysteine, thiourea and thiosulfate. Examination revealed that the coloration was due to the substitution of a water molecule in the complex for sulfur-containing anions. The color develops instantaneously, except in the case of thiosulfate where it is rather slow. In order to elucidate the nature of the color reaction, a kinetic examination has been conducted.

Experimental

Preparation of Aquahydrogen(ethylenediaminetetraacetato)ruthenium(III), [Ru(Hedta)(H₂O)]. The method of Mukaida *et al.*[3)] has been modified as follows. Ruthenium(IV) oxide (5 mmol, Japan Engelhard Co., Ltd.) was dissolved in concd HCl and after repeated heating to dryness on a water bath the residue was dissolved in concd HCl (20 ml). To the solution was added EDTA (5.3 mmol, free acid) and the mixture heated to dryness several times. From a 6 M HCl solution of the residue, $H[RuCl_2(H_2edte)] \cdot 5H_2O$ crystallized out. The recrystallized solid was dissolved in water and the solution added with an equimolar amount of NaOH and evaporated to dryness twice. On the addition of ethanol, a yellow solid precipitated which was dissolved in water and the solution repeatedly evaporated. This lead to the crystallization of $[Ru(Hedta)(H_2O)]$ (yield; 60%). The purity of the complex was checked by alkalimetric titration.

Other Chemicals. All chemicals used were "special grade" from Wako Chemicals Co. and purified by recrystallization or distillation when necessary. Twice-distilled water was used throughout the experiments.

Kinetics and Equilibrium Measurements. The majority of the measurements were conducted at 30 °C and an ionic strength of 0.1. Since perchlorate, nitrate and chloride react slowly with $[Ru(Hedta)(H_2O)]$, the pH and ionic strength of the solution were adjusted by adding calculated amounts of buffer solutions (acetate, phosphate, carbonate and borate buffers). Care was taken to avoid the possible photochemical oxidation of the complex solution.[2)]

The buffered solutions of either reactant, thermostated separately in the dark, were mixed together, and the mixture transferred to a 10 mm path quartz cell. The increase in the optical density of the solution at 495 nm was followed on a spectrophotometer at constant temperature. The pseudo-first order rate constant, k_{obsd}, was evaluated by plotting $\log (D_\infty - D_t)$ against time t, where D_t and D_∞ are the optical densities at time t and infinity, respectively.

Physical Measurements. The electronic spectra and the color development were recorded on a Hitachi 124 spectrophotometer with an attached thermostatted cell compartment. CD spectra were obtained by a JASCO J20 recording spectrophotometer and IR spectra on a JASCO 403G infrared spectrophotometer. The magnetic susceptibility was measured on a Gouy magnetic balance and the pH on a Toa Denpa Digital pH meter, Type HM-8 and HM-20B.

Results and Discussion

Color Reaction. Of the sulfur compounds investigated, it was found that alkanethiols, cysteine, phenylmethanethiol, *O*-ethyl dithiocarbonate, diethyldithiocarbamate, thiourea and thiosulfate gave pink to reddish brown colors, while the benzenethiols gave blue colors. Sulfides and disulfides did not react at all. It may be noted that there is a parallel between this color reaction and the iodine-azide reaction of thiols and thiocarbonyl compounds.[4)]

As may be seen from Fig. 1, the mole ratio of the ruthenium(III) complex to sulfur compound was found to be 1: 1.

The colored mixture of the complex and cysteine gave

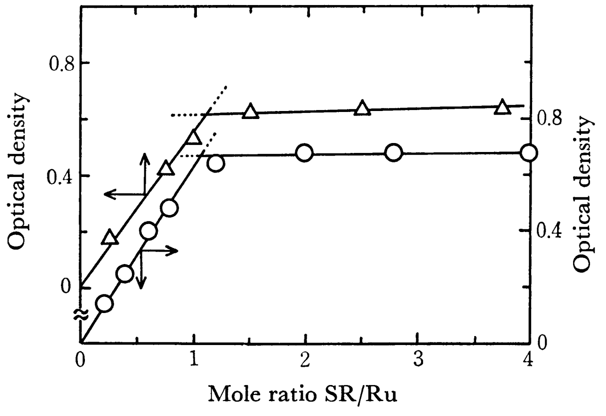

Fig. 1. Mole ratio plot.
$[Ru(Hedta)(H_2O)]$: 2.0×10^{-4} M.
—△—: $S_2O_3^{2-}$; —○—: cysteine.

new CD peaks at 516 nm (+0.64), 436 nm (−0.41), 380 nm (+0.25) and 335 nm (−0.33) where the figures in parentheses represent $\Delta\varepsilon$ values. The reaction products were paramagnetic in both solution and solid states. The magnetic moment of ruthenium in the colored solution (0.1 M Ru) was calculated as; $\mu_{eff}=$ 1.91 B.M. at 24.2 °C and therefore it may be said that the +3 state of Ru is retained throughout the reaction. The existence of Ru–carboxylate bonding was confirmed by a strong infrared absorption band at 1620 cm^{-1}. In addition, the elemental analysis of the colored solid gave the atomic ratio C/N as 4.20, which may be compared to the calculated value 4.33 for a 1 : 1 complex of Ru–EDTA and cysteine.

On the basis of these observations, it has been assumed that the color reaction is an anation reaction of the following type;

$$Ru(edta)(H_2O)^- + SR^{n-} \rightleftarrows Ru(edta)(SR)^{(n+1)-} + H_2O, \quad (1)$$

where SR denotes a sulfur-containing compound. The nature of the color change may be a charge transfer between sulfur and ruthenium(III) in the complex.

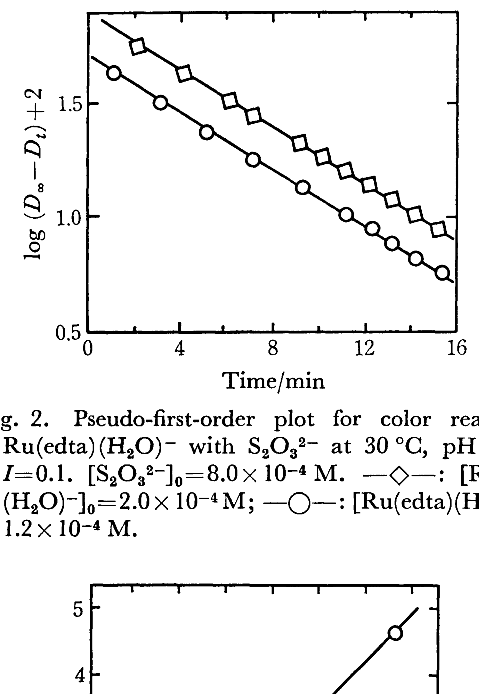

Fig. 2. Pseudo-first-order plot for color reaction of $Ru(edta)(H_2O)^-$ with $S_2O_3^{2-}$ at 30 °C, pH 4.7 and I=0.1. $[S_2O_3^{2-}]_0=8.0\times10^{-4}$ M. —◇—: $[Ru(edta)(H_2O)^-]_0=2.0\times10^{-4}$ M; —○—: $[Ru(edta)(H_2O)^-]_0=1.2\times10^{-4}$ M.

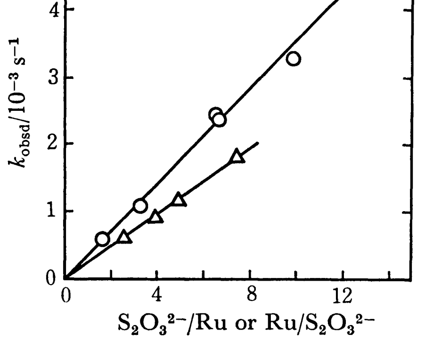

Fig. 3. Dependence of k_{obsd} on the concentration of the excess reactants.

—○—: $S_2O_3^{2-}$ is excess; $[Ru(edta)(H_2O)^-]_0=1.2\times10^{-4}$ M; —△—: $Ru(edta)(H_2O)^-$ is excess; $[S_2O_3^{2-}]_0=0.8\times10^{-4}$ M.

Kinetics of Thiosulfate Anation. Of the various sulfur compounds investigated, the color reaction of thiosulfate is relatively slow and the rate could be followed photometrically. The reaction is first order in each reactant (Fig. 2) and the rate is independent of the hydrogen ion concentration in the pH range 4—6. Figure 3 illustrates the dependence of k_{obsd} on the concentration of the excess reactant, thiosulfate or Ru(III)–EDTA complex. A linear relationship is seen to hold in both cases. From the slopes of these straight lines, the rate constant, k_{AN}, of the thiosulfate anation has been evaluated as;

$$k_{AN} = 2.94 \pm 0.11\ M^{-1}\ s^{-1} \text{ at } 30\ ^\circ C \text{ and } I = 0.1.$$

In the presence of an excess of thiosulfate ($[S_2O_3]$/[Ru–EDTA]=6.7), the Arrhenius plot of k_{obsd} at 22, 30, and 40 °C gave the activation energy as, $E_a=37\pm2$ kJ mol^{-1}.

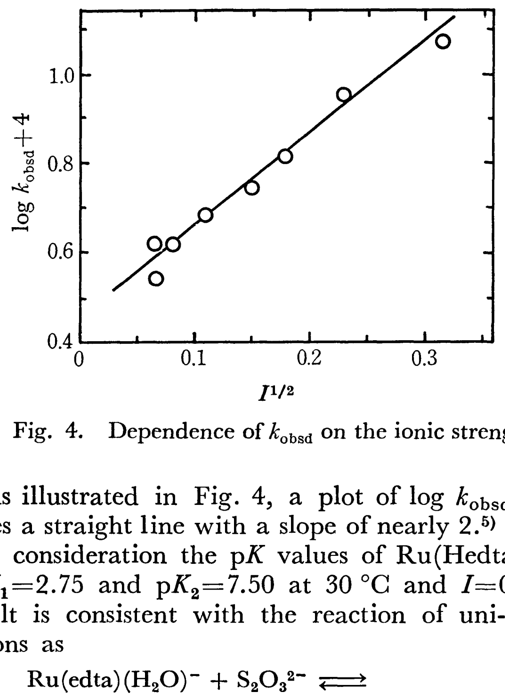

Fig. 4. Dependence of k_{obsd} on the ionic strength.

As illustrated in Fig. 4, a plot of log k_{obsd} *vs.* $I^{1/2}$ gives a straight line with a slope of nearly 2.[5)] Taking into consideration the pK values of $Ru(Hedta)(H_2O)$ (pK_1=2.75 and pK_2=7.50 at 30 °C and I=0.1) this result is consistent with the reaction of uni-bivalent anions as

$$Ru(edta)(H_2O)^- + S_2O_3^{2-} \rightleftarrows Ru(edta)(S_2O_3)^{3-} + H_2O. \quad (2)$$

The value of the rate constant for this reaction is surprisingly large compared with the halide anation of ruthenium(III)–ethylenediamine and related complexes ($k_{AN}\approx10^{-3}\ M^{-1}\ s^{-1}$).[6)] However, it has been noted before that substitution reactions at the sixth coordination site of quinquedentate EDTA complexes of Cr(III) and related complexes are remarkably fast.[7,8)] Similar labilizing effect due to quinquedentate EDTA may be expected for $Ru(edta)(H_2O)^-$.

In the kinetic measurements, k_{obsd} increased linearly with increase in the thiosulfate concentration up to 0.1 M, the concentration range investigated here and no saturation of the rate was observed. Consequently it is not possible to anticipate further the mechanism of the anation.

As reported earlier, the rate of color development is independent of $[H^+]$ in the pH range 4—6. However,

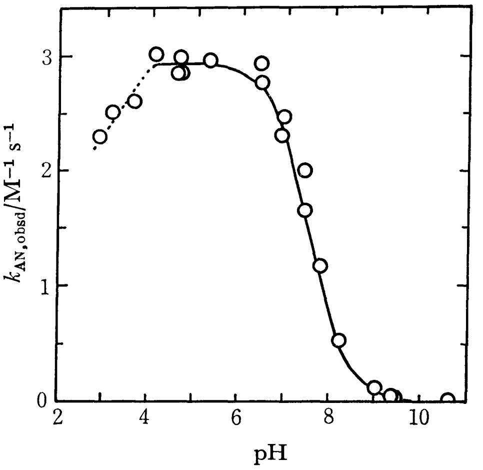

Fig. 5. Dependence of $k_{AN,obsd}$ on pH of the solutions. ○: experimental point; —: calculated curve.

it was found in the region of pH 6—10 that the rate decreases with increase in pH, as illustrated in Fig. 5. (Experimental points are shown by open circles). Since the pK_2 of Ru(Hedta)(H_2O) is known to have the value of 7.50, this result is expected to arise from the decrease in the concentration of the aqua complex with increase in pH. This leads to

$$k_{AN,obsd} = (k_{AN}+k'_{AN}K_2/[H^+])/(1+K_2/[H^+]),$$

where $k_{AN,obsd}$ denotes the observed rate constant in the range pH>≈6 and k_{AN} and k_{AN} are the anation rate constants for Ru(edta)(H_2O)$^-$ and Ru(edta)(OH)$^{2-}$, respectively. Substituting the values, $k_{AN}=2.94\ M^{-1}\ s^{-1}$, $k'_{AN}\approx 0$ and $K_2=10^{-7.50}$ M, the values of $k_{AN,obsd}$ as a function of pH have been calculated and the results plotted in Fig. 5 (solid line). The agreement between experimental and calculated values is satisfactory.

In the pH range<4, $k_{AN,obsd}$ decreases with increase in [H^+]. This may be explained by considering the participation of the less reactive protonated complex, Ru(Hedta)(H_2O) in the reaction, thus

$$k_{AN,obsd} = (k_{AN}+k''_{AN}[H^+]/K_1)/(1+[H^+]/K_1+K_2/[H^+]),$$

where k''_{obsd} refers to the anation rate constant for Ru(Hedta)(H_2O). The evaluation of k''_{AN} from the rate data in the acidic range (pH<4) is, however, difficult owing to the possible decomposition of the thiosulfate in acidic solution.

Equilibrium Study. In the higher pH range (pH>≈8), it was found that the optical densities at infinite time decrease as illustrated in Fig. 6. This may be ascribed to the existence of the following equilibrium;

$$Ru(edta)(S_2O_3)^{3-} + OH^- \rightleftarrows Ru(edta)(OH)^{2-} + S_2O_3^{2-} \qquad (3)$$

At 495 nm the only colored species is Ru(edta)$(S_2O_3)^{3-}$ with a molar extinction coefficient, ε, at this wavelength of $3.13\times10^3\ M^{-1}\ cm^{-1}$. Using the spectral data of

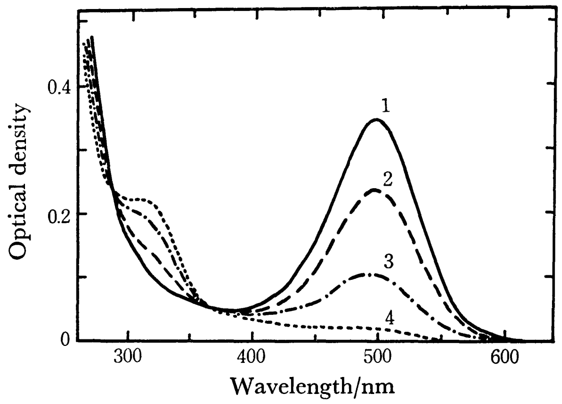

Fig. 6. Change of absorption spectra in the higher pH region.
1: pH 8.57, 2: pH 9.29, 3: pH 9.91, 4: pH 10.81.

Fig. 6, the equilibrium constant (K_{eq}) for Reaction 3 has been calculated as; $K_{eq}=19.1$ at 30 °C and $I=0.1$. Since the pK_2 value for Ru(Hedta)(H_2O) is known, the equilibrium constant (K_{AN}) for the thiosulfate anation (Reaction 2) may be calculated using the following relationship:

$$K_{AN} = [Ru(edta)(S_2O_3)^{3-}]/[Ru(edta)(H_2O)^-][S_2O_3^{2-}]$$
$$= K_2/K_{eq}\cdot K_w,$$

where K_w denotes the ionic product of water. Substituting the values; $K_2=10^{-7.50}$, $K_{eq}=10^{1.28}$ and $K_w=10^{-13.8}$;

$$\log K_{AN} = 5.02 \text{ at } 30\ ^\circ C \text{ and } I = 0.1.$$

This value may be compared with that estimated from the spectral data in the mole ratio plot of the optical densities in Fig. 1 (log K_{AN}=5.16).

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