1370 © *1990 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***63***, *1370—1373 (1990)* [Vol. 63, No. 5

Kinetics of the Ligand Substitution Reactions of a Labilized Ruthenium(III) Complex, [Ru{*N*′-(2-hydroxyethyl)ethylenediamine-*N*,*N*,*N*′-triacetate}(H_2O)]

Hiroshi Ogino,* Tetsuo Katsuyama,† and Setsuo Ito
Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980
†Department of Basic Technology, Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992

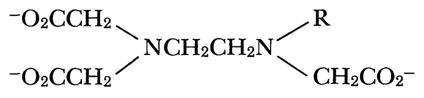
(Received December 4, 1989)

The kinetics of the substitution reactions of [*N*′-(2-hydroxyethyl)ethylenediamine-*N*,*N*,*N*′-triacetato]-aquaruthenium(III), [Ru(hedtra)(H_2O)], with X (Br^-, CH_3CN, SCN^-, and pyridine) to give [RuX(hedtra)] were carried out at 25 °C and I=0.5 mol dm^{-3}. The substitution reactions were found to be unusually rapid. The rate constants of the forward reaction (k_f) and of the backward reaction (k_b) were $k_f=0.13\pm0.01$ mol^{-1} dm^3 s^{-1} and $k_b=(1.9\pm0.2)\times10^{-2}$ s^{-1} for the reaction with Br^-, $k_f=0.48\pm0.02$ mol^{-1} dm^3 s^{-1} and $k_b=(3.0\pm0.2)\times10^{-2}$ s^{-1} for the reaction with CH_3CN, and $k_f=7.5\pm0.2$ mol^{-1} dm^3 s^{-1} and $k_b=(1.3\pm0.8)\times10^{-2}$ s^{-1} for the reaction with SCN^-, respectively. The kinetics of the reaction of [Ru(hedtra)(H_2O)] with py was studied as a function of pH. The observed rate constants of the reaction were separated into two rate constants; the rate constant of the forward reaction of [Ru(hedtra)(H_2O)] with py (18 ± 2 mol^{-1} dm^3 s^{-1}) and that of [Ru(OH)(hedtra)]$^-$ with py (3.0 ± 1.0 mol^{-1} dm^3 s^{-1}). The mechanisms of the reactions are discussed.

Chromium(III)-EDTA and several *N*-substituted ethylenediamine-*N*,*N*′,*N*′-triacetatochromium(III) complexes [CrL(H_2O)] have been shown to undergo unusually rapid ligand substitution reactions with several anions X (Eq. 1),[1–5]

$$[\mathrm{CrL(H_2O)}] + \mathrm{X} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [\mathrm{CrXL}] + \mathrm{H_2O} \qquad (1)$$[6]

L =



where the ligand L contains a pendant group R having coordinating ability, i.e. $CH_2CO_2^-$, CH_2CO_2H, CH_2CH_2OH, CH_2OCOCH_3, or $CH_2CO_2Co(NH_3)_5^{2+}$. The remarkable labilization effect has been explained by postulating that the transient coordination of the pendant group R assists the elimination of the coordinated water molecule in the forward reaction or the ligand X in the backward reaction. Matsubara and Creutz demonstrated that the ligand substitution reactions of [Ru(edta)(H_2O)]$^-$ (Eq. 2) are much faster than those of [Ru(NH_3)$_5$(H_2O)]$^{3+}$ [7,8] and proceed via an associative route.

$$[\mathrm{Ru(edta)(H_2O)}]^- + \mathrm{X} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [\mathrm{RuX(edta)}]^- + \mathrm{H_2O} \qquad (2)$$

They postulated that hydrogen bonding between the coordinated water and the pendant carboxylate group distorts all of the metal–ligand bonds so that a very open area is created adjacent to the hydrogen bonding. In this way the hydrogen bonding may sterically activate [Ru(edta)(H_2O)]$^-$ towards associative substitution. Therefore, the mechanism is different from the one proposed by us for the chromium(III) complexes.[2–4]

In the present paper, the kinetics of the reactions of [Ru(hedtra)(H_2O)] with NCS^-, Br^-, CH_3CN (AN), and pyridine (py) are investigated (Eq. 3), in order to know

$$[\mathrm{Ru(hedtra)(H_2O)}] + \mathrm{X} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [\mathrm{RuX(hedtra)}] + \mathrm{H_2O} \qquad (3)$$

whether the remarkable reactivity of [Ru(edta)(H_2O)]$^-$ is attributable to the hydrogen bonding[8] or the transient coordination of the pendant group to the ruthenium(III) center, as proposed for the chromium(III) complexes.[2–5]

Hydrogen bonding between the coordinated water and non-charged *N*′-(2-hydroxyethyl) group in [Ru(hedtra)(H_2O)] should be much weaker than that in [Ru(edta)(H_2O)]$^-$. Therefore, if hydrogen bonding is responsible for the high reactivity of [Ru(edta)(H_2O)]$^-$, [Ru(hedtra)(H_2O)] might be expected to show much lower reactivity than that of [Ru(edta)(H_2O)]$^-$. A part of the present work has been reported in our review very briefly.[4] Quite recently, Bajaj and van Eldik reported a kinetic study of reaction 3.[9]

Experimental

Measurements. Electronic spectra were recorded on a Union-Giken SM-401 spectrophotometer. The kinetics were carried out at 25.0±0.1 °C and I=0.5 M ($NaClO_4$) under pseudo-first-order conditions:[10] concentrations of X greatly exceeded those of [Ru(hedtra)(H_2O)]. The rapid reactions were followed with a Union-Giken RA-401 stopped-flow spectrophotometer and the slow reactions, with the Union-Giken SM-401 spectrophotometer. The plots of $\ln|A_t - A_\infty|$ vs. time were linear for at least 3 half-lives, where A_t and A_∞ represent the absorbances at time t and infinity, respectively.

The acid dissociation constant of reaction 4

$$[\mathrm{Ru(hedtra)(H_2O)}] \overset{K_a}{\rightleftharpoons} \mathrm{H^+} + [\mathrm{Ru(hedtra)(OH)}]^- \qquad (4)$$

was determined as $pK_a=5.11\pm0.03$ at 25.0±0.1 °C and I=0.10 M ($NaClO_4$). The measurements of pH were made with a Toa

TSC 10-A pH stat, which was calibrated against standard perchloric acid solutions. The pK_a value obtained is in a good agreement with that reported by Bajaj and van Eldik.[9]

Preparation of Na[RuCl(hedtra)]·H$_2$O. $RuCl_3 \cdot nH_2O$ containing 44% Ru (3 g) was dissolved in 30 ml of water. To the solution was added 1 ml of concentrated HCl. This solution was evaporated to dryness on a boiling water bath. H$_3$hedtra (4.2 g) dissolved in 30 ml of hot water was added to the residue. The resulted solution was evaporated to dryness. The residue was then dissolved in 20 ml of water and the pH of the solution was adjusted to 2 with 0.5 M NaOH solution. The solution was refluxed for 3 h and evaporated to dryness. A yellowish brown mass was washed with 5 ml portions of cold water repeatedly which afforded a yellow powder.

The powder of the desired product was filtered off, washed with ethanol and ether, and air-dried. Found: C, 26.46; H, 3.86; N, 6.42%. Calcd for Na[RuCl(hedtra)]·H$_2$O: C, 26.53; H, 3.78; N, 6.19%.

Preparation of H[RuBr(hedtra)]·2.5H$_2$O. Na[RuCl(hedtra)]·H$_2$O was dissolved in a minimum amount of water. One third volume of concentrated HBr was added to the solution. Then, ethanol–ether mixture (5:1) was added slowly until the solution became turbid. Upon standing the solution for several hours at room temperature, the desired product was obtained as orange crystals which were filtered off, washed with ethanol and ether, and air-dried. Found: C, 24.24; H, 4.22; N, 5.55%. Calcd for H[RuBr(hedtra)]·2.5H$_2$O: C, 23.91; H, 4.20; N, 5.58%.

Results

Electronic Spectra. When Na[RuCl(hedtra)]·H$_2$O is dissolved in water, the absorption maxima appear at 233 nm (ε=3340, shoulder), 282 nm (ε=1950), and 350 nm (ε=834, shoulder). H[RuBr(hedtra)]·2.5H$_2$O shows almost identical absorption maxima to those of Na[RuCl(hedtra)]·H$_2$O, i.e. 233 nm (ε=3400, shoulder) and 282 nm (ε=1930). This suggests that both complexes are rapidly converted in water to a common species having the same chromophore, namely [Ru(hedtra)(H$_2$O)]. This is further supported by the observation that the kinetics of the ligand substitution reactions of both complexes showed almost identical results. Similar behavior to this has been reported for [Ru(edta)(H$_2$O)]$^-$: [RuCl(Hedta)]$^-$ and [RuCl$_2$(H$_2$edta)]$^-$ liberate chloride ions rapidly in dilute aqueous solutions.[11]

Kinetics of the Ligand Substitution Reactions of [Ru(hedtra)(H$_2$O)] with NCS$^-$, Br$^-$, AN, and py. When an aqueous solution of Na[RuCl(hedtra)]·H$_2$O was mixed with a solution containing excess NaSCN, two consecutive reactions were observed. The observed spectral changes and rates of the reactions were essentially identical when H[RuBr(hedtra)]·2.5H$_2$O was used in place of Na[RuCl(hedtra)]·H$_2$O. This implies that when these two complexes are dissolved in water, [Ru(hedtra)(H$_2$O)] is formed very rapidly. The first reaction completed within several seconds after mixing. The second reaction was much slower than the first (Fig. 1). A similar phenomenon to this was observed for the reaction of [Ru(edta)(H$_2$O)]$^-$ with NCS$^-$ and it was concluded that the first reaction corresponds to the formation of [Ru(NCS)(edta)]$^{2-}$ and the second, to that of [Ru(NCS)$_2$(edta)]$^{3-}$.[8] In the first reaction of [Ru(hedtra)(H$_2$O)] with NCS$^-$, the absorption maximum appears at 465 nm (ε=1300) after completion of the reaction (Fig. 1 curve B). This is a quite similar value to that of [Ru(NCS)(edta)]$^{2-}$ (λ_{max}=460 nm (ε=1010)). Therefore, the first reaction is attributed to the occurrence of reaction 3, where X=NCS$^-$. The reaction obeyed a first-order rate law

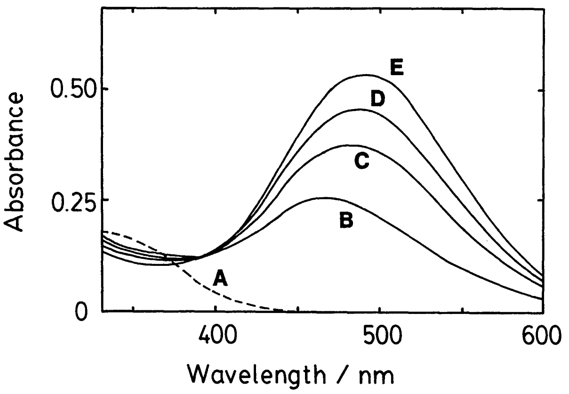


Fig. 1. Spectral change of the reaction of [Ru(hedtra)(H$_2$O)] (1.98×10^{-4} M) with SCN$^-$ (0.500 M) at [H$^+$]=1.81×10^{-3} M. Dotted line (curve A) denotes the spectrum of 1.98×10^{-4} M [Ru(hedtra)(H$_2$O)] in the absence of SCN$^-$ and curve B, that measured immediately after mixing (the spectrum shows the complete formation of [Ru(NCS)(hedtra)]$^-$). Curves C–E denote the spectra obtained 10, 20, and 50 min, respectively, after mixing.

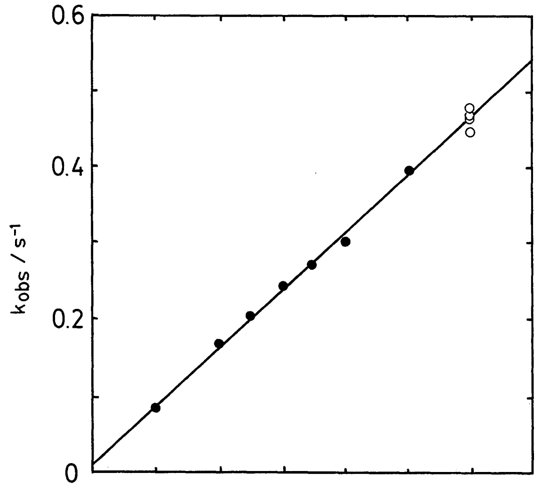


Fig. 2. Plot of the observed pseudo-first-order rate constants (k_{obsd}) vs. [SCN$^-$] in the reaction of [Ru(hedtra)(H$_2$O)] with SCN$^-$. H[RuBr(hedtra)]·2.5H$_2$O (solid circles) and Na[RuCl(hedtra)]·H$_2$O (open circles) were used as the source of [Ru(hedtra)(H$_2$O)]. The pHs of the solutions were varied from 2.01 to 4.06.

Table 1. Equilibrium and Rate Constants for the Ligand Substitution of $[Ru(hedtra)(H_2O)]$ (Eq. 3) and $[Ru(edta)(H_2O)]^-$ (Eq. 2)

Ligand	$k_f/M^{-1}\,s^{-1}$	k_b/s^{-1}	K/M^{-1}
		$[Ru(hedtra)(H_2O)]$ system[a)]	
Br^-	0.13 ± 0.01	$(1.9\pm0.2)\times10^{-2}$	6.6 ± 1.0
CH_3CN	0.48 ± 0.02	$(3.0\pm0.2)\times10^{-2}$	$16\ \pm2$
SCN^-	$7.5\ \pm0.2$	$(1.3\pm0.8)\times10^{-2}$	$580\ \pm200$
	$6.5\ \pm0.3$[b)]	—	—
py	$18\quad\pm2$[c)]	—	$\gg3\times10^3$
		$[Ru(edta)(H_2O)]^-$ system[d),e)]	
CH_3CN	30 ± 7	$3.2\ \pm0.2$	9 ± 3
SCN^-	270 ± 20	$0.5\ \pm0.1$	540 ± 100
py	6300 ± 500	0.061 ± 0.002	$(1.0\pm0.3)\times10^5$

a) At 25 °C and I=0.5 M. b) From Ref. 9. c) The forward rate constant of the reaction of $[Ru(OH)(hedtra)]^-$ with py (k_f') was $3.0\pm1.0\ M^{-1}\,s^{-1}$. d) From Ref. 8. e) At 25 °C and I=0.2 M.

under pseudo-first-order conditions. The observed pseudo-first-order rate constants (k_{obsd}) were independent of the concentrations of the complex (5.4×10^{-5}—3.9×10^{-4} M) and pH (2.01—4.06). As shown in Fig. 2, the plot of the k_{obsd} values against the concentrations of NCS^- gives a good linear relation with an intercept. This kinetic behavior indicates that the reaction 3 is reversible and thus the slope and intercept values of the plot correspond to the forward (k_f) and backward (k_b) rate constants, respectively, and the ratio of the slope and intercept values, to the equilibrium constant (K) for the process. The kinetic and equilibrium data are listed in Table 1.

Shepherd et at. prepared and isolated $K[Ru(NCS)_2(H_2edta)]$.[12)] The absorption maximum of the species was reported to appear at 486 nm (ε=2700). The spectral change observed for the second reaction of $[Ru(hedtra)(H_2O)]$ with NCS^- (Fig. 1) is consistent with the occurrence of the following reaction:

$$[Ru(NCS)(hedtra)]^- + NCS^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Ru(NCS)_2(hedtra)]^{2-} \tag{5}$$

The kinetic study of this slower second reaction was also carried out under pseudo-first-order conditions. The values of k_2 and k_{-2} were determined to be $(2.5\pm1.2)\times10^{-4}\ M^{-1}\,s^{-1}$ and $(1.0\pm0.1)\times10^{-3}\ s^{-1}$, respectively.

Thiocyanate ions react with $[Ru(hedtra)(H_2O)]$ to give $[Ru(NCS)(hedtra)]^-$ and $[Ru(NCS)_2(hedtra)]^{2-}$. However, when $X=Br^-$, AN, and py, only the formation of $[RuX(hedtra)]^{n-}$ (n=1 for Br^- and n=0 for AN and py) was observed. The kinetic and equilibrium data for the reactions of $[Ru(hedtra)(H_2O)]$ with Br^- and AN are given in Table 1. The reaction of $[Ru(hedtra)(H_2O)]$ with py (Eq. 3) leads to complete formation of $[Ru(hedtra)(py)]$ under the present experimental conditions. The equilibrium constant (K) of the reaction was estimated to be $K\gg3\times10^3\ M^{-1}$ at 25 °C. Therefore, the plots of the observed pseudo-first-order rate constants (k_{obsd}) vs. [py] show very minor intercepts. The k_{obsd} values were found to be acid-dependent in the pH range 5.1—6.1. This kinetic behavior is compatible with the reaction scheme given in Eqs. 6 and 7:

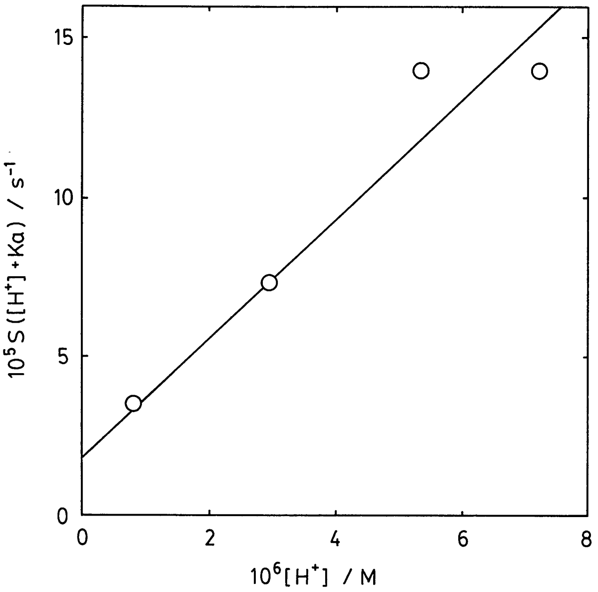


Fig. 3. Plot of $S([H^+]+K_a)$ vs. $[H^+]$ for the reaction of $[Ru(hedtra)(H_2O)]$ with py. $Na[RuCl(hedtra)]\cdot H_2O$ was used as the source of $[Ru(hedtra)(H_2O)]$.

$$\begin{array}{ll} [Ru(hedtra)(H_2O)] + py \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [Ru(hedtra)(py)] + H_2O & \\ -H^+ \Big\downarrow\Big\uparrow +H^+ \qquad K_a & (6) \\ [Ru(OH)(hedtra)]^- + py \underset{k_b'}{\overset{k_f'}{\rightleftharpoons}} [Ru(hedtra)(py)] + OH^- & \\ & (7) \end{array}$$

From the mechanism, the following equation can be derived,

$$S = \frac{k_f[H^+] + k_f'K_a}{[H^+] + K_a} \tag{8}$$

where S denotes the slope of the plots of the k_{obsd} values vs. [py] at a given pH. As expected from Eq. 8, the plot of $S([H^+]+K_a)$ vs. $[H^+]$ gave a linear relation (Fig. 3). From the slope and intercept values, the k_f and k_f' values were determined. The kinetic and equilibrium data are listed in Table 1.

Discussion

The equilibrium constants of Eq. 3 (K) which are the formation constants of [RuX(hedtra)] are listed in Table 1. The numerical value of each K resembles that of the corresponding EDTA complex.[8] The K values appear to correlate with the basicity of ligand X.

As compared in Table 1, the rate constant of the reaction of [Ru(hedtra)(H_2O)] with NCS^- determined in this work is in good agreement with the value reported by Bajaj and van Eldik.[9]

Recently, Bajaj and van Eldik carried out a kinetic study of the reaction of $[Ru(edta)(H_2O)]^-$ with several ligands.[13] They concluded that the hydrogen bonding between the coordinated water and the free carboxylate oxygen is responsible for the high lability of the water molecule. This can either results in the creation of an open space or labilize the coordinated water molecule.[13] However, the internal hydrogen bonding does not weaken the ruthenium(III)-OH_2 bond, but rather *strengthens* it and thus sould *retard* the rate. On the other hand, the transient coordination of the pendant carboxylate or N'-(2-hydroxyethyl) group to a central metal ion weakens the metal-OH_2 bond.

As shown in Table 1, the anation and aquation rate constants of $[Ru(edta)(H_2O)]^-$ are larger by 40—400 times than those of [Ru(hedtra)(H_2O)]. However, even the ligand substitution of [Ru(hedtra)(H_2O)] is unusually rapid. The aquation rate constant of $[RuBr(hedtra)]^-$ is larger by 10^4 times than that of $[RuBr(NH_3)_5]^{2+}$ ($8.7\times10^{-7}\ s^{-1}$).[14] Therefore, [Ru(hedtra)(H_2O)] and $[Ru(edta)(H_2O)]^-$ are considered to be labilized mainly by the transient coordination of the pendant group R (CH_2COO^- or CH_2CH_2OH) to the ruthenium(III) center.

References

1) Abbreviations used in this work: ethylenediamine-N,N,N',N'-tetraacetate=edta^{4-}, N'-(2-hydroxyethyl) ethylenediamine-N,N,N'-triacetate=hedtra^{3-}.

2) H. Ogino, T. Watanabe, and N. Tanaka, *Inorg. Chem.*, **14**, 2093 (1975).

3) H. Ogino, M. Shimura, and N. Tanaka, *Inorg. Chem.*, **18**, 2497 (1979).

4) H. Ogino and M. Shimura, *Adv. Inorg. Bioinorg. Mech.*, **4**, 107 (1985) and references cited therein.

5) H. Ogino, A. Masuko, S. Ito, N. Miura, and M. Shimura, *Inorg. Chem.*, **25**, 708 (1986).

6) Charges are omitted for simplicity.

7) T. Matsubara and C. Creutz, *J. Am. Chem. Soc.*, **100**, 6255 (1978).

8) T. Matsubara and C. Creutz, *Inorg. Chem.*, **18**, 1956 (1979).

9) H. C. Bajaj and R. van Eldik, *Inorg. Chem.*, **28**, 1980 (1989).

10) 1 M=1 mol dm^{-3}.

11) N. A. Ezerskaya and T. D. Solovyka, *Russ. J. Inorg. Chem.*, **11**, 991 (1966).

12) J. Guardalabene, S. Gulnac, N. Keder, and R. E. Shepherd, *Inorg. Chem.*, **18**, 22 (1979).

13) H. C. Bajaj and R. van Eldik, *Inorg. Chem.*, **27**, 4052 (1988).

14) J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, **11**, 47 (1974).