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Aquoruthenium(II) Catalysis of Substitution on Aquoruthenium(III)

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The kinetics of $Ru(H_2O)_6^{2+}$-catalyzed substitution of Cl^-, Br^-, and I^- onto $Ru(H_2O)_6^{3+}$ have been investigated spectrophotometrically. The reactions followed zero-order kinetics in Ru^{3+} for up to 60% of the absorbance change and pseudo-zero-order rate constants obeyed the rate law $d[RuX^{2+}]/dt = k_X[Ru^{2+}][X^-][Ru^{3+}]^0$, where $k_X = (8.5 \pm 0.2) \times 10^{-3}\ M^{-1}\ sec^{-1}$, $(10.2 \pm 0.2) \times 10^{-3}\ M^{-1}\ sec^{-1}$, and $9.8 \pm 0.4\ M^{-1}\ sec^{-1}$ for $X^- = Cl^-$, Br^-, and I^- at 25° and $\mu = 0.30$ M in HBF_4 media. The rates of reaction were independent of $[H^+]$ from 0.112 to 0.292 M. The experimental rate law requires a catalytic mechanism where substitution on $Ru(H_2O)_6^{2+}$ is rate determining. Activation enthalpies for all three reactions were within the range 19.8 ± 0.4 kcal mol^{-1}. This suggests that substitution occurs by a dissociative process.

Normally slow substitution reactions of Cr(III),[1] Ru(III),[2,3] and other cations are known to be catalyzed by lower oxidation states of the same metals. This "redox catalysis" may involve both substitution on the catalyst species and electron transfer between the two oxidation states of the metal. When the reduced form is labile, information about the electron-transfer step can be obtained. However, if the electron-transfer process is rapid, the same sort of reaction could give information about the lability of the reduced form of the metal ion. We now report a study of the kinetics of the reactions

$$Ru(H_2O)_6^{3+} + Ru(H_2O)_6^{2+} + X^- \rightleftarrows Ru(H_2O)_5X^{2+} + Ru(H_2O)_6^{2+} + H_2O$$

where X^- is Cl^-, Br^-, or I^-. The kinetics of these catalyzed Ru(III) substitution reactions provide detailed information about substitution reactions of Ru(II).[4]

Experimental Section

Materials.—Stock solutions of $Ru(H_2O)_6^{3+}$ and of $Ru(H_2O)_6^{2+}$ were prepared by chromatographic separation of the products of reduction of RuO_4. (Hereafter, coordinated waters will be omitted.) These preparations represent adaptations of the methods of Cady and Connick[5a] and Mercer and Buckley,[5b] respectively.

Millimole quantities of $K_2RuCl_5(H_2O)$ or RuI_3 were digested in 6 ml of concentrated sulfuric acid until their solution was substantially free of halide ion and oxalic acid was added until the solution had changed to a pale yellow color. The resulting solution was diluted with 20 ml of 1 M H_2SO_4 and oxidized with a mixture of 5 g of $K_2S_2O_8$ and 0.1 g of Ag_2CO_3 at 60–70°. Nitrogen was used to sweep volatile RuO_4 from the reaction mixture into a Dry Ice–ethanol cold trap. RuO_4 obtained from the millimole samples of starting material was dissolved in 50 ml of 2 F HBF_4 and reduced by stirring the solution with 5 g of 30 mesh granular tin for 4 hr under nitrogen or argon.

When Ru^{2+} was desired, the reduced solution was used to charge a cation-exchange column after dilution to 500 ml with oxygen-free 0.5% HF. The column was then washed with 100 ml of 0.1 F HBF_4 which contained 5 ml of 50% HF, and the red Ru^{2+} band was eluted with 1.0 F HBF_4 at a flow rate of 1 ml/min. CO_2 or argon blankets were used to exclude oxygen during all operations and the ruthenium(II) fraction was collected in a serum-capped flask of CO_2. This fraction, 40 ml of a $(10–15) \times 10^{-3}$ M solution, was stored frozen under argon.

When the Ru^{3+} ion was the desired product, the reduced solution was filtered and bubbled with oxygen for 30 min prior to dilution and ion exchange. The charged column was washed with 50 ml of 0.25 M HCl and rinsed with 50 ml of 0.1 F HBF_4, and the pale yellow Ru^{3+} band was eluted with 1.0 F HBF_4 at a flow rate of 1.0 ml/min. This fraction, 200 ml of a $(3–4) \times 10^{-3}$ M solution, was stored in polyethylene bottles in the frozen state.

A 2-cm diameter, 15 cm long column of Dowex 50W-X2, 100–200 mesh, hydrogen ion form, cation-exchange resin was used in both separations.

$RuCl^{2+}$, $RuBr^{2+}$, and RuI^{2+} were prepared by treating 11.0 ml of a 4.6×10^{-3} M Ru^{3+} solution which was 0.055 M in X^- with 1.0 ml of 10^{-2} M Ru^{2+} solution for 1.5 hr under argon. The reaction mixtures were quenched with 50 ml of water and were used to charge a 2-cm diameter, 5 cm long cation-exchange column. The complexes were eluted as discrete bands with 0.5 F HBF_4 and 25–30 ml of a 5×10^{-4} M solution of each was obtained. The same species could also be isolated from the solutions of the rate determinations.

The ruthenium concentrations of the stock solutions were determined using the method of Gortsema and Cobble.[6] These results were checked using Woodheld and Fletcher's method[7] and results were found to agree within 0.5%.

The purity of stock solutions of Ru^{2+} and Ru^{3+} was verified polarographically.[8] No evidence was found to indicate tin(II) or tin(IV) contamination and the extent of aquoruthenium(III) contamination of ruthenium(II) solutions was estimated to be less than 1%. This estimate was verified by titrating fresh solutions with standard triiodide solutions to a starch–I_2 end point. An additional check of the reproducibility of the stock solutions was provided by substituting granular lead for tin in the reduction of RuO_4. The visible and uv spectra and polarographic characteristics of the species obtained by the two methods were identical.

Solutions used in rate determinations were prepared from reagent grade HBF_4, HCl, NaBr, and NaI. All solutions were prepared using triply distilled water and solutions containing the iodide ion were stored under argon to prevent oxidation to I_3^-. Sodium iodide solutions were standardized iodometrically after oxidation to I_2 by NO_2^- in 0.1 N HCl. NBF_4 solutions were standardized by diluting aliquots until their pH was the same as that of standard 0.1 N $HClO_4$.

Polarographic measurements were made at the dme using a Sargent XV polarograph or at a hanging mercury drop using a Heath EUA-19-2 and associated apparatus. Voltammograms were measured at 34 mV/sec.

Rate Determinations.—Rate determinations were performed in 1.00-cm silica cells situated in the constant-temperature block of a Cary 14 spectrophotometer. Rate measurements were made at 315, 385, and 530 nm for the catalytic formation of RuX^{2+} where X = Cl, Br, and I, respectively. Prior to each run 3.0 ml of a solution containing ligand and Ru^{3+} were deaerated with argon in a serum-capped cell for 15 min. The cell was then placed in the block for a 20-min temperature equilibration period. Agreement of the spectrum of the solution before and after this period served as an indication of the absence of catalytic impurities. To initiate the substitution reaction 0.20 ml of

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[3] J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 437 (1965).

[4] T. W. Kallen and J. E. Earley, *Chem. Commun.*, 851 (1970).

[5] (a) H. H. Cady and R. E. Connick, *J. Amer. Chem. Soc.*, **80**, 2646 (1958); (b) E. E. Mercer and R. R. Buckley, *Inorg. Chem.*, **4**, 1692 (1965).

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[7] J. L. Woodheld and J. M. Fletcher, *J. Chem. Soc.*, 5039 (1961).

[8] R. R. Buckley and E. E. Mercer, *J. Phys. Chem.*, **70**, 3103 (1966).

temperature-equilibrated Ru^{2+} stock solution was introduced by syringe and the cell was inverted several times.

Absorbance at the wavelength of maximum absorption of RuX^{2+} increased linearly with time. This behavior, characteristic of zero-order reactions, persisted for up to 60% of the total absorbance change. Since halide concentrations and both Ru^{2+} and RuX^+ concentrations remain constant during the reaction

$$\frac{1}{\Delta\epsilon}\frac{dA}{dt} = \frac{d}{dt}[\mathrm{RuX}^{2+}] = k$$

where $\Delta\epsilon$ is the difference between the molar absorptivities of RuX^{2+} and Ru^{3+}. Pseudo-zero-order rate constants were therefore evaluated using graphic values of dA/dt and predetermined values of $\Delta\epsilon$ at the various temperatures.

Results

Table I summarizes spectral and electrochemical data for the various species involved in this study. Our Ru(II) solutions were more transparent in the uv region than those studied by Mercer and Buckley.[5] They observed an absorption minimum near 350 nm with ϵ 21 while our solutions had a minimum at 310 with ϵ 0.5. We obtained solutions of ruthenium(II) similar to theirs by stirring aquoruthenium(III) solutions in 1.0 *F* HBF_4 with tin under nitrogen rather than under argon or CO_2.[9]

TABLE I

HALF-WAVE POTENTIALS AND SPECTRAL CHARACTERISTICS OF RUTHENIUM SPECIES IN HBF_4 AT 25°

Complex	μ, *M*	$E_{1/2}$, V *vs.* nhe	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
$Ru(H_2O)_6^{2+}$	1.0	0.21 (A)[a,b]	392	10.8
			535	9.0
$Ru(H_2O)_6^{3+}$	1.0	0.21[a]	225	2480
			392	30.4
$Ru(H_2O)_5Cl^{2+}$	0.3	0.08[c]	317	661
$Ru(H_2O)_5Br^{2+}$	0.3	0.10[c]	385	536
			305 sh	
$Ru(H_2O)_5I^{2+}$	0.3	0.10[c]	290	1530
			460 sh	
			530	534

[a] μ = 0.1 *M* in *p*-toluenesulfonic acid, dme. [b] Anodic wave. [c] Estimated cyclic voltammetrically as $E_{1/2} \approx {}^1/_2(E^{ox}_{max} + E^{red}_{max})$. Peak separations were 64, 61, and 64 mV for X^- = Cl^-, Br^-, and I^-, respectively.

The spectrum of $RuCl^{2+}$ is the same as that previously reported,[4] but we observed an additional peak for Ru^{3+} at 392 nm. This maximum is the same in 1.0 *F* HBF_4 and 1.0 *M* *p*-toluenesulfonic acid and is a real feature of the aquo ion. The magnitude of its molar absorptivity suggests a d–d transition.

The spectra of RuX^{2+} species resemble those of $Ru(NH_3)_5X^{2+}$[10] species except that the lowest energy bands (presumably ligand → metal charge transfer) are higher in energy for RuX^{2+} and molar absorptivities are about one-third those of the ammine complexes.

Solution nmr measurements using Evans' method[11] demonstrated that $Ru(H_2O)_6^{2+}$ is diamagnetic.

The equilibrium constant for the formation of $RuCl^{2+}$ was estimated by catalytically equilibrating argon-deaerated solutions of the Ru^{3+} ion and Cl^- with small quantities of Ru^{2+}. Solution compositions were computed from absorbance readings at 315 nm after 75 hr, assuming that only Ru^{3+}, $RuCl^{2+}$, Ru^{2+}, and $RuCl^+$ were present. The results for a series of such equilibrations, at $[Cl^-]$ = 1–5 m*M*, led to

$$K_1^{III} = \frac{[\mathrm{RuCl}^{2+}]}{[\mathrm{Ru}^{3+}][\mathrm{Cl}^-]} = 148 \pm 6\ M^{-1}$$

The data of Connick and Fine[12] may be used to compute $\log K_2^{III} = 1.2$ and $\log K_3^{III} = 0.4$ at $\mu = 0.3$ *M*. Therefore the concentration of $RuCl_2^+$ represents from 1 to 6% of the $RuCl^{2+}$ concentration and $RuCl_3$ is present in negligible quantities at equilibrium in the range of chloride concentrations used in these determinations.

The half-wave potentials of Table I may be used to estimate $\log (K_1^{III}/K_1^{II}) = 2.2 \pm 0.1$ by assuming equal diffusion coefficients for the oxidized and reduced species. Therefore, K_1^{II}, the formation constant of $RuCl^+$, is estimated to be $1.0 \pm 0.3\ M^{-1}$.

Table II lists observed zero-order rate constants for Ru^{2+}-catalyzed formation of RuX^{2+} and second-order rate constants calculated on the basis of the rate law

TABLE II

KINETIC DATA FOR THE Ru^{2+}-CATALYZED FORMATION OF RuX^{2+}[a]

$[X^-]$, *M*	10^4[Ru(II)], *M*	10^4[Ru(III)], *M*	$[H^+]$, *M*	Temp, °C	10^7k, *M* sec^{-1}	10^3k_1, M^{-1} sec^{-1}
(A) $X^- = Cl^-$						
0.020	6.69	13.0	0.292	25.0	1.13 ± 0.01	8.41
0.020	6.69	8.68	0.292	25.0	1.16 ± 0.03	8.67
0.040	6.69	8.68	0.292	25.0	2.24 ± 0.04	8.34
0.060	6.69	8.68	0.292	25.0	3.38 ± 0.06	8.42
0.080	6.69	8.68	0.292	25.0	4.62 ± 0.06	8.64
0.100	7.19	7.55	0.112	25.0	5.98 ± 0.09	8.32
0.100	7.19	7.55	0.194	25.0	6.13 ± 0.04	8.52
0.100	7.19	7.55	0.292	25.0	6.17 ± 0.02	8.58
0.100	6.69	8.68	0.292	25.0	5.63 ± 0.11	8.42
0.100	4.45	8.68	0.292	25.0	3.66 ± 0.02	8.24
0.100	3.27	8.68	0.292	25.0	2.76 ± 0.10	8.44
0.100	2.10	8.68	0.292	25.0	1.74 ± 0.07	8.28
					Av	8.5 ± 0.2
0.020	6.69	13.0	0.292	20.0	0.588 ± 0.002	4.40
0.020	6.69	13.0	0.292	30.0	1.92 ± 0.02	14.3
0.020	6.69	13.0	0.292	35.0	3.41 ± 0.04	25.5
(B) $X^- = Br^-$						
0.025	4.36	7.55	0.194	25.0	1.10 ± 0.07	10.1
0.025	6.28	7.55	0.194	25.0	1.67 ± 0.06	10.6
0.050	6.28	7.55	0.194	25.0	3.24 ± 0.03	10.3
0.075	5.53	8.30	0.194	25.0	4.29 ± 0.09	10.3
0.075	6.28	7.55	0.194	25.0	4.84 ± 0.02	10.2
0.100	5.53	8.30	0.194	25.0	5.49 ± 0.18	9.9
0.100	6.28	7.55	0.194	25.0	6.22 ± 0.26	9.9
					Av	10.2 ± 0.2
0.025	3.84	8.07	0.194	20.0	0.517 ± 0.005	5.4
0.025	4.36	7.55	0.194	30.0	1.91 ± 0.02	17.6
0.025	4.36	7.55	0.194	35.0	3.36 ± 0.08	30.8
(C) $X^- = I^-$						
0.025	5.53	8.30	0.194	25.0	1.42 ± 0.01	10.2
0.050	5.53	8.30	0.194	25.0	2.77 ± 0.03	10.0
0.075	5.53	8.30	0.194	25.0	4.26 ± 0.04	10.3
0.100	5.53	8.30	0.194	25.0	5.22 ± 0.09	9.4
0.100	6.28	7.55	0.194	25.0	5.43 ± 0.29	9.1
					Av	9.8 ± 0.4
0.025	6.83	7.55	0.194	20.0	0.98 ± 0.05	5.8
0.025	6.83	7.55	0.194	30.0	3.06 ± 0.06	18.0
0.025	6.83	7.55	0.194	35.0	5.24 ± 0.08	30.8

[a] μ = 0.30 *M*, HBF_4–$NaBF_4$ media.

$$\frac{d}{dt}[\mathrm{RuX}^{2+}] = k_1[\mathrm{Ru}^{2+}][\mathrm{Ru}^{3+}]^0[\mathrm{X}^-]$$

The hydrogen ion dependence of the catalytic reaction was negligible in the interval $0.112\ M \geq [H^+] \geq$

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[9] Careful separation of these products by chromatography gave small quantities of a second species having elution characteristics which were similar to those of the aquoruthenium(II) ion but having a broad visible maximum at 418 nm ($\epsilon \approx 300$) and a shoulder in the uv region ($\epsilon \approx 1500$, λ 220 nm).

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[12] R. E. Connick and D. A. Fine, *J. Amer. Chem. Soc.*, **83**, 3414 (1961).

0.292 M. For reactions in which $X^- = Cl^-$ this rate law fits the data within experimental error but for the bromide and iodide cases there is some tendency for k_1 to decrease at higher halide concentrations. The data taken at 25° were fitted to the alternative rate law

$$[Ru^{2+}]/k = 1/k' + 1/k'K[X^-]$$

giving the results shown in Table III.

TABLE III

KINETIC PARAMETERS FOR THE HALIDE DEPENDENCE OF k AT 25°[a]

X^-	$10^3k'$, sec^{-1}	K, M^{-1}	$10^3k'K$, M^{-1} sec^{-1}
Cl^-	(12)[b]	(0.7 ± 0.3)[c]	8.5 ± 0.2
Br^-	12 ± 5	0.9 ± 0.4	10.9 ± 0.2
I^-	11 ± 4	1.0 ± 0.3	10.5 ± 0.2

[a] $\mu = 0.30$ M (HBF_4–$NaBF_4$); $[H^+] = 0.292$ M for Cl^-, 0.194 M for Br^- and I^-; $k/[Ru^{2+}] = k'K[X^-]/(1 + K[X^-])$. [b] Assumed. [c] Calculated from $k_1 = k'K$ and assumed k'.

Activation parameters, based on the simple second-order rate law are tabulated in Table IV.

TABLE IV

ACTIVATION PARAMETERS FOR THE Ru^{2+}-CATALYZED FORMATION OF RuX^{2+} [a]

X^-	$\Delta H^{\ddagger}$,[b] kcal mol^{-1}	$\Delta S^{\ddagger}$,[b] eu
Cl^-	20.2 ± 0.3	-0.4 ± 0.4
Br^-	19.8 ± 0.4	-1.2 ± 1.5
I^-	19.5 ± 0.7	-2.4 ± 2.2

[a] Conditions as in Table III. [b] At 20.0–35.0°.

Discussion

The observed rate laws require the mechanism

$$Ru^{2+} + X^- \xrightleftharpoons[k_2]{k_1} RuX^+$$

$$RuX^+ + Ru^{3+} \xrightleftharpoons[k_4]{k_3} RuX^{2+} + Ru^{2+}$$

where k_3 and k_4 are much larger than k_1 and k_2. During the initial portion of the reaction, where k_4 is unimportant and successive formation of higher order halo complexes may be neglected, the observed rate is independent of [Ru(III)] and $d[RuX^{2+}]/dt = k_1[Ru^{2+}][X^-]$. This analysis requires that the product $k_3[Ru^{3+}]$ be at least one order of magnitude greater than k_2. It is therefore possible to place a conservative lower limit on the rate of the electron-transfer reaction as $k_3 > 10^2$ M^{-1} sec^{-1}.[13]

The measured activation enthalpies for all three reactions are consistent with this interpretation. In each case $\Delta H^{\ddagger}$ is similar to that reported for other Ru(II) substitution reactions[14–16] and is much larger than $\Delta H^{\ddagger}$ values reported for Ru(II)–Ru(III) electron-transfer reactions.[13,16] Variational trends may be observed in the activation parameters which parallel the variation of the corresponding parameters for association of the halides with $Co(NH_3)_6^{3+}$,[17,18] and the trend of $-\Delta S^{\ddagger}$ parallels the increase in entropy of the solvated anion in the series X = Cl, Br, I.[19] However, the lack of more significant variation of the kinetic parameters with X implies a common rate-determining process which is predominantly dissociative.

The alternative rate law described by the parameters of Table III refers to a mechanism in which water is initially lost from the Ru^{2+} coordination sphere. The rate of water exchange of Ru^{2+} may be identified as $6k'$ of this mechanism and estimated as 10^{-1} sec^{-1}. Since the diamagnetism of Ru^{2+} indicates a t_{2g}^6 configuration, this value may be best compared with 3×10^{-8} sec^{-1} for water exchange of the t_{2g}^6 Rh(III) aquo ion under similar conditions.[20] A similar variation is found with charge in the water-exchange rates of the d^3 V(II) and Cr(III) aquo ions.

Connick's estimate of the rate constant for aquation of $RuCl^{2+}$ ($k \approx 10^{-8}$ sec^{-1} at 25°)[21] and our estimate of K_1^{III} may be used to compute the rate constant for the uncatalyzed formation of $RuCl^{2+}$ as 10^{-6} M^{-1} sec^{-1}. Similar data[22,23] lead to $k = 5 \times 10^{-5}$ M^{-1} sec^{-1} for the rate of uncatalyzed formation of $Ru(NH_3)_5Cl^{2+}$. Our data indicate that Ru^{2+} is more labile than these t_{2g}^5 Ru(III) species by a factor of 10^4.

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(13) This estimate is consistent with the rate of self-exchange in the $Ru(NH_3)_6^{2+}$–$Ru(NH_3)_6^{3+}$ system reported by T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).

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