Electron-Transfer Reactions Involving the Aquoruthenium(II)–Aquoruthenium(III) Couple

WOLFHART BÖTTCHER, GILBERT M. BROWN, and NORMAN SUTIN*

Rate constants in CF_3SO_3H at 25 °C have been determined for the oxidation of $Ru(H_2O)_6^{2+}$ by $Ru(NH_3)_5py^{3+}$, $Ru(NH_3)_5isn^{3+}$, $Co(phen)_3^{3+}$, $Fe(H_2O)_6^{3+}$, $Os(bpy)_3^{3+}$, and $Ru(bpy)_3^{3+}$ and for the reduction of $Ru(H_2O)_6^{3+}$ by $Ru(NH_3)_6^{2+}$, $V(H_2O)_6^{2+}$, and $Ru(H_2O)_5Cl^+$. The application of the Marcus equations to these reactions leads to an estimate of $(6 \pm 4) \times 10^1$ M^{-1} s^{-1} for the rate constant of the $Ru(H_2O)_6^{2+}$–$Ru(H_2O)_6^{3+}$ exchange reaction. The rates of the $Fe(H_2O)_6^{2+}$–$Fe(H_2O)_6^{3+}$, $Ru(H_2O)_6^{2+}$–$Ru(H_2O)_6^{3+}$, and $Ru(NH_3)_6^{2+}$–$Ru(NH_3)_6^{3+}$ exchange reactions are discussed, and it is shown that $(a_2 - a_3)$, the difference in the radii of the two oxidation states of the couples, may be related to $(S°_{Red} - S°_{Ox})$, the difference in the hydration entropies of the two oxidation states. These considerations suggest a relatively large difference (~ 0.1 Å) between the ruthenium–oxygen bond lengths in $Ru(H_2O)_6^{2+}$ and $Ru(H_2O)_6^{3+}$. Replacement of a coordinated water molecule by a chloride ion dramatically increases the aquoruthenium(II)–aquoruthenium(III) exchange rate. The reaction of $Ru(H_2O)_5OH^{2+}$ with $Cr(H_2O)_6^{2+}$ proceeds by an inner-sphere mechanism, and the rate constants for the formation and dissociation of the hydroxide-bridged intermediate have been determined.

Despite the apparent simplicity of electron-exchange processes, the rate constants for electron exchange between 2+ and 3+ aquo ions of the first transition series span a very wide range: from less than 2×10^{-5} M^{-1} s^{-1} for the $Cr(H_2O)_6^{2+}$–$Cr(H_2O)_6^{3+}$ couple to ~ 5 M^{-1} s^{-1} for the $Fe(H_2O)_6^{2+}$–$Fe(H_2O)_6^{3+}$ and $Co(H_2O)_6^{2+}$–$Co(H_2O)_6^{3+}$ couples.[1] Some, but by no means all, of the factors responsible for these rate variations are understood.[1-11] For purposes of comparison with the couples of the first transition series, we have estimated the rate constant for the $Ru(H_2O)_6^{2+}$–$Ru(H_2O)_6^{3+}$ exchange reaction by measuring the rates of a number of electron-transfer reactions in which the ruthenium couple is involved. The reactions studied are the oxidation of $Ru(H_2O)_6^{2+}$ by $Ru(NH_3)_5py^{3+}$, $Ru(NH_3)_5isn^{3+}$, $Co(phen)_3^{3+}$, $Fe(H_2O)_6^{3+}$, $Os(bpy)_3^{3+}$, and $Ru(bpy)_3^{3+}$ and the reduction of $Ru(H_2O)_6^{3+}$ by $Ru(NH_3)_6^{2+}$, $Cr(H_2O)_6^{2+}$, $V(H_2O)_6^{2+}$, and $Ru(H_2O)_5Cl^+$.[12] The electron-exchange rate of the ruthenium couple was calculated from these rate constants by using the Marcus equations[4,6,7]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad (1)$$

$$\log f_{12} = (\log K_{12})^2 / (4 \log (k_{11}k_{22}/Z^2)) \qquad (2)$$

where k_{12} and K_{12} are the rate and equilibrium constants for the cross reaction, respectively, k_{11} and k_{22} are the exchange rates of the aquoruthenium couple and its reaction partner, respectively, and Z is the collision frequency of two uncharged particles in solution (taken as 10^{11} M^{-1} s^{-1}). Some of the assumptions and limitations inherent in the above equations have recently been reviewed.[9,13] It was found that reasonable exchange-rate estimates can be obtained with eq 1 and 2 provided that the driving force for the cross reaction is not too large.[9]

Experimental Section

Materials. Trifluoromethanesulfonic acid (CF_3SO_3H, 3M Co.) was distilled twice (bp 54 °C (8 torr)) and diluted with triply distilled water. A stock solution of its lithium salt was prepared from equivalent amounts of CF_3SO_3H and recrystallized lithium carbonate. Solutions containing $Ru(H_2O)_6^{3+}$ were prepared from ruthenium trichloride (Johnson Matthey) by using a modification of a previously described procedure.[14] The chloride was removed by fuming 0.2 g of $RuCl_3\cdot3H_2O$ twice with 15 mL of concentrated H_2SO_4 to a final volume of about 2 mL. The resulting slurry was dissolved in 100 mL of H_2O, and then 0.1 g of Ag_2CO_3 and 5 g of $K_2S_2O_8$ were added and the mixture was heated to 60–70 °C on a water bath. The volatile RuO_4 was carried through a glass tube into a second vessel by argon. The RuO_4 was dissolved there in 50 mL of 2 M CF_3SO_3H and reduced to $Ru(H_2O)_6^{2+}$ by granular tin. After oxidation by O_2, the resulting $Ru(H_2O)_6^{3+}$ solution was purified by ion-exchange chromatography (Dowex 50W-X2, H form, elution with 1.0 M CF_3SO_3H). Stock

solutions of $Ru(H_2O)_6^{3+}$ in 1.0 M CF_3SO_3H were kept frozen at -80 °C. For the reduction to $Ru(H_2O)_6^{2+}$, a known amount of the $Ru(H_2O)_6^{3+}$ solution was deaerated by argon and about 10% less than the equivalent quantity of a $Cr(H_2O)_6^{2+}$ solution was added. The freshly prepared $Ru(H_2O)_6^{2+}$ solutions were standardized spectrophotometrically (ϵ 9.0 M^{-1} cm^{-1} at 535 nm and 10.8 M^{-1} cm^{-1} at 392 nm)[14] and were generally used immediately. Solutions of $Ru(H_2O)_6^{3+}$ which had "aged" were repurified by chromatography as before. Solutions containing $Ru(H_2O)_5Cl^{2+}$ were prepared as described by Seewald, Sutin, and Watkins[15] by using CF_3SO_3H instead of $HClO_4$ as the eluting acid. $Ru(H_2O)_5Cl^+$ was generated by H_2/Pt-black reduction of $Ru(H_2O)_5Cl^{2+}$ in mixtures of CF_3SO_3H and HCl. Since the equilibrium for the reaction

$$Ru(H_2O)_5Cl^+ + H_2O = Ru(H_2O)_6^{2+} + Cl^-$$
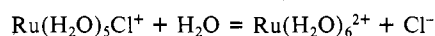
is only 1.0 ± 0.3 M,[14] high chloride concentrations (0.1–0.2 M in the reactant solutions) were needed to obtain appreciable concentrations of $Ru(H_2O)_5Cl^+$. Fortunately the loss of Cl^- from $Ru(H_2O)_5Cl^+$ is slow enough ($k = 8.5 \times 10^{-3}$ s^{-1})[14] to allow its electron-transfer reactions to be studied by the stopped-flow technique without interference from the dissociation reaction.

The starting material for the $Cr(H_2O)_6^{2+}$ stock solution was CrO_3 (Baker Analytical Reagent). This was dissolved in CF_3SO_3H and reduced to chromium(III) by H_2O_2 and further to $Cr(H_2O)_6^{2+}$ by amalgamated zinc under an argon atmosphere. Solutions containing $V(H_2O)_6^{2+}$ in 1.0 M CF_3SO_3H were prepared by dissolving V_2O_5 in CF_3SO_3H followed by reduction with amalgamated zinc. This preparation was checked kinetically by the reduction of $Co(phen)_3^{3+}$ with $V(H_2O)_6^{2+}$ ($k = 3.8 \times 10^3$ M^{-1} s^{-1}).[16] $[Co(phen)_3](ClO_4)_3$ was synthesized following the method of Pfeiffer and Werdelmann.[17] Perchlorate was replaced by trifluoromethanesulfonate by ion-exchange chromatography (Dowex 50W-X2, H^+ form). The eluted $Co(phen)_3^{3+}$ solutions were checked spectrophotometrically (ϵ 99 M^{-1} cm^{-1} at 450 nm, 3.7×10^3 M^{-1} cm^{-1} at 350 nm, and 4.68×10^3 M^{-1} cm^{-1} at 330 nm)[16] and used immediately. Stock solutions of iron(III) were prepared by dissolving iron wire of high purity in excess CF_3SO_3H. The resulting $Fe(H_2O)_6^{2+}$ was oxidized to $Fe(H_2O)_6^{3+}$ with H_2O_2, which was subsequently removed by boiling. The iron concentration of the stock solution was determined spectrophotometrically as $Fe(phen)_3^{2+}$ (ϵ 1.1×10^4 M^{-1} cm^{-1} at 510 nm) after the addition of ascorbic acid. The CF_3SO_3H concentration was determined by an ion-exchange method.

$[Ru(NH_3)_5py](ClO_4)_2$ and $[Ru(NH_3)_5isn](ClO_4)_2$ were synthesized according to literature procedures.[18] Solutions containing these Ru(II) salts in 1.0 M CF_3SO_3H were prepared shortly prior to use, and, when necessary, a little less than equivalent amount of $Fe(H_2O)_6^{3+}$ was added to oxidize the Ru(II) to Ru(III). The $CF_3SO_3^-$ salt of hexaammineruthenium(III) was prepared as follows. Commercially available $[Ru(NH_3)_6]Cl_3$ (Johnson Matthey) was recrystallized twice from dilute hydrochloric acid and dissolved in dilute CF_3SO_3H; a solution prepared from equivalent amounts of CF_3SO_3H and Ag_2CO_3 was then added dropwise until AgCl precipitation was complete. The solution was filtered, and a few drops of 3 M CF_3SO_3H were added

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Table I. Second-Order Rate Constants for Reactions Involving the Aquoruthenium(II)–Aquoruthenium(III) Couple in 1.0 M Trifluoromethanesulfonic Acid at 25 °C

reaction	$\Delta E°$, V^a	k_{12}, $M^{-1} s^{-1}$	k_{22}, $M^{-1} s^{-1}$	k_{11}, ^{b} $M^{-1} s^{-1}$
$Ru(H_2O)_6^{2+} + Ru(NH_3)_5py^{3+}$	0.082^c	1.1×10^4	4.7×10^5 ^{c}	1.5×10
$Ru(H_2O)_5Cl^+ + Ru(H_2O)_6^{3+}$	0.131^d	3.0×10^3		
$Ru(NH_3)_6^{2+} + Ru(H_2O)_6^{3+}$	0.150^e	1.4×10^4	2×10^4 ^{k,l}	3.2×10
$Ru(H_2O)_6^{2+} + Co(phen)_3^{3+}$	0.15^f	5.3×10	40^m	2.4×10^{-1} ^{k}
$Ru(H_2O)_6^{2+} + Ru(NH_3)_5isn^{3+}$	0.167^c	5.5×10^4	4.7×10^5 ^{c}	1.4×10
$V(H_2O)_6^{2+} + Ru(H_2O)_6^{3+}$	0.472^g	2.8×10^2	1×10^{-2} ^{n,l}	3.7×10^{-1}
$Ru(H_2O)_6^{2+} + Fe(H_2O)_6^{3+}$	0.52^h	2.3×10^3	4.2^o	1.2×10^{-2}
$Ru(H_2O)_6^{2+} + Os(bpy)_3^{3+}$	0.60^i	2.9×10^8	2×10^9 ^{p}	2.3×10^{-1}
$Ru(H_2O)_6^{2+} + Ru(bpy)_3^{3+}$	1.04^j	1.9×10^9	2×10^9 ^{q,r}	2.5×10^{-2} ^{r}
$Ru(NH_3)_6^{2+} + Ru(H_2O)_5Cl^{2+}$	0.064^e	$\sim 2 \times 10^5$	2×10^4 ^{k,l}	9.2×10^5
$V(H_2O)_6^{2+} + Ru(H_2O)_5Cl^{2+}$	0.341^g	1.7×10^3	1×10^{-2} ^{n,l}	1.2×10^3

^{a} Potential difference calculated by using +0.217 and +0.086 V for $E°$ of the $Ru(H_2O)_6^{3+,2+}$ and $Ru(H_2O)_5Cl^{2+,+}$ couples, respectively. ^{b} Calculated exchange rate of the aquoruthenium(II)–aquoruthenium(III) couple. ^{c} M. Abe, G. M. Brown, H. J. Krentzien, and H. Taube, submitted for publication. ^{d} This work. ^{e} Reference 22. ^{f} Reference 9. ^{g} W. M. Latimer, "Oxidation Potentials", Prentice-Hall, Englewood Cliffs, NJ, 1952, p 260. ^{h} E. H. Swift, "A System of Chemical Analysis", Prentice-Hall, New York, 1949, p 542. ^{i} E. P. Dwyer, N. A. Gibson, and E. C. Gyarfas, *J. Proc. R. Soc. N. S. W.*, 84, 80 (1950). ^{j} C.-T. Lin, W. Böttcher, M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, 98, 6536 (1976). ^{k} T. J. Meyer and H. Taube, *Inorg. Chem.*, 7, 2639 (1968). ^{l} Corrected to 1.0 M ionic strength. ^{m} H. M. Neumann, quoted in R. Farina and R. G. Wilkins, *Inorg. Chem.*, 7, 514 (1968). ^{n} K. V. Krishnamurty and A. C. Wahl, *J. Am. Chem. Soc.*, 80, 5921 (1958). ^{o} J. Silverman and R. W. Dodson, *J. Phys. Chem.*, 56, 846 (1952). ^{p} Assumed equal to $Ru(bpy)_3^{2+}-Ru(bpy)_3^{3+}$ exchange rate. ^{q} R. C. Young, F. R. Keene, and T. J. Meyer, *J. Am. Chem. Soc.*, 99, 2468 (1977). ^{r} Corrected for the effects of diffusion control according to $1/k_{act} = 1/k_{obsd} - 1/k_{diff}$ by using $k_{diff} = 3.2 \times 10^9$ M^{-1} s^{-1}.

to the filtrate to precipitate the trifluoromethanesulfonate salt. This was filtered, recrystallized twice from dilute CF_3SO_3H, and dried. Weighed amounts of the solid were dissolved in dilute CF_3SO_3H, and the ruthenium(III) concentration was determined spectrophotometrically (ϵ 10^2 M^{-1} cm^{-1} at 320 nm and 478 M^{-1} cm^{-1} at 275 nm).[19] For the reduction to $Ru(NH_3)_6^{2+}$, a less than equivalent amount of Eu^{2+}(aq) (made from Eu_2O_3, CF_3SO_3H, and amalgamated zinc) was added to the $Ru(NH_3)_6^{3+}$, and the $Ru(NH_3)_6^{2+}$ solutions were used immediately.[20] [Ru(bpy)₃]Cl₂ was obtained from the G. F. Smith Co., and [Os(bpy)₃]I₂ was synthesized according to literature procedures. Both materials were recrystallized from water and checked by elemental analysis before being converted into their trifluoromethanesulfonate salts.

Kinetic Measurements. The reduction of $Co(phen)_3^{3+}$ by $Ru(H_2O)_6^{2+}$ was followed on a Cary 17 spectrophotometer. The runs were carried out in 10-cm cells with $Ru(H_2O)_6^{2+}$ in at least tenfold excess. The other reactions were studied by use of a modified Durrum D-110 stopped-flow spectrophotometer.[21] Either the kinetic data were digitized and punched on computer cards or they were stored in a Biomation Model 8100 transient recorder and printed on tape. The kinetic analyses were performed on a CDC 7600 computer. In the $Ru(H_2O)_6^{3+}-Cr(H_2O)_6^{2+}$ system the reductant was always in more than tenfold excess. The acid concentration varied between 0.05 and 1.0 M, and the ionic strength was maintained at 1.0 M by the addition of lithium trifluoromethanesulfonate. Kinetic measurements were made at 15.0, 25.0, and 35.0 °C. In the other redox reactions studied, one of the reactants was always in at least tenfold excess, and the reaction mixture contained 1.0 M $CF_3SO_3^-$.

The $Ru(bpy)_3^{3+}-Ru(H_2O)_6^{2+}$ and $Os(bpy)_3^{3+}-Ru(H_2O)_6^{2+}$ reactions were studied by using a flash-lamp-pumped dye laser (Phase R, Model DL-110) to form $*Ru(bpy)_3^{2+}$ or $*Os(bpy)_3^{2+}$ in the presence of $Ru(H_2O)_6^{3+}$. The quenching of the excited $M(bpy)_3^{2+}$ by $Ru(H_2O)_6^{3+}$ produces $M(bpy)_3^{3+}$ and $Ru(H_2O)_6^{2+}$. These species react in a second reaction to re-form $M(bpy)_3^{2+}$ and $Ru(H_2O)_6^{3+}$. Since no $Ru(H_2O)_6^{2+}$ was present initially, the reaction of $M(bpy)_3^{3+}$ with $Ru(H_2O)_6^{2+}$ followed equal-concentration second-order kinetics.

Electrochemical Measurements. A PAR Model 173 potentiostat and Model 175 universal programmer were used for cyclic voltammetry. Potentials were measured at a hanging drop Hg electrode vs. SCE at 25 °C. The pH dependence of the $E_{1/2}$ of the $Ru(H_2O)_6^{3+,2+}$ couple was determined from cyclic voltammetry measurements on a solution of the Ru(II) complex.

Results

Kinetics. The reaction between $Ru(H_2O)_5Cl^+$ and $Ru(H_2O)_6^{3+}$ was studied under conditions in which excess $Ru(H_2O)_6^{2+}$ was initially present. A plot of k_{obsd} vs. the concentration of $Ru(H_2O)_6^{3+}$ at constant concentrations of $Ru(H_2O)_5Cl^+$ and $Ru(H_2O)_6^{2+}$ was linear with a zero in-

tercept. This result and a consideration of the formal reduction potentials of the reactants (see below) indicate that no correction for the reverse reaction between $Ru(H_2O)_6^{2+}$ and $Ru(H_2O)_5Cl^{2+}$ was necessary. The rate was also independent of [Cl⁻] in the range 0.05–0.1 M. An anomalous feature of the reaction between $Ru(H_2O)_5Cl^+$ and $Ru(H_2O)_6^{3+}$ was an initial fast component which varied with the preparations of $Ru(H_2O)_6^{3+}$. The amount of the fast component appeared to correlate with the residence time of $Ru(H_2O)_6^{3+}$ on the ion-exchange column. The fast component is probably due to the oxidation of $Ru(H_2O)_5Cl^+$ by small amounts of polymeric Ru(III) aquo ions present in solution. Apart from the reaction of $Ru(H_2O)_5Cl^+$ with $Ru(H_2O)_6^{3+}$, which was the only reaction studied with $Ru(H_2O)_6^{3+}$ in excess, and the oxidation of $Cr(H_2O)_6^{2+}$ by $Ru(H_2O)_6^{3+}$, which is discussed further below, all of the reactions investigated obeyed good second-order kinetics, first order in each reactant. A summary of the various rate constants is presented in Table I. The rate constant for the reduction of $Ru(H_2O)_5Cl^{2+}$ by $V(H_2O)_6^{2+}$ determined in this work is in good agreement with the value previously determined in $HClO_4$ medium.[15] The activation parameters for the $Ru(H_2O)_6^{2+}-Fe(H_2O)_6^{3+}$ and $Ru(H_2O)_6^{2+}-Os(bpy)_3^{3+}$ reactions are $\Delta H^\ddagger = 6.8 \pm 1$ kcal mol^{-1} and $\Delta S^\ddagger = -20 \pm 3$ cal deg^{-1} mol^{-1} and $\Delta H^\ddagger = -0.6 \pm 0.4$ kcal mol^{-1} and $\Delta S^\ddagger = -22 \pm 2$ cal deg^{-1} mol^{-1}, respectively.

The reaction of $Ru(H_2O)_6^{3+}$ with $Cr(H_2O)_6^{2+}$ proceeds via an intermediate that absorbs between 320 and 400 nm. At 330 nm the molar absorptivity of this rapidly appearing and slowly decaying intermediate is 420 ± 30 M^{-1} cm^{-1}. (This value is based on the initial ruthenium concentration.) The rate of formation of the intermediate is given by

$$d[I]/dt = b[Cr(H_2O)_6^{2+}][Ru(H_2O)_6^{3+}][H^+]^{-1}$$

with $b = (9.5 \pm 0.9) \times 10^3$ s^{-1} at 25 °C. The activation parameters for this reaction are $\Delta H^\ddagger = 11.0 \pm 0.2$ kcal mol^{-1} and $\Delta S^\ddagger = -3.3 \pm 0.6$ cal deg^{-1} mol^{-1}. The rate of disappearance of the intermediate is described by

$$-d[I]/dt = (c + d[H^+])[I]$$

with $c = 0.03 \pm 0.02$ s^{-1} and $d = 1.6 \pm 0.1$ M^{-1} s^{-1} at 25 °C. The parameters for the acid-dependent pathway are $\Delta H^\ddagger = 10.0 \pm 0.2$ kcal mol^{-1} and $\Delta S^\ddagger = -24 \pm 1$ cal deg^{-1} mol^{-1}.

Electrochemistry. Formal potentials for the $Ru(H_2O)_6^{3+,2+}$ and $Ru(H_2O)_5Cl^{2+,+}$ couples were estimated by cyclic voltammetry at 25 °C in a 1.0 M CF_3SO_3H medium. The

reduction potentials for the two couples are +0.217 and +0.086 V vs. NHE respectively. These values are based on E_f = +0.066 V[22] for the $Ru(NH_3)_6^{3+,2+}$ couple. In addition the pK_a for the equilibrium

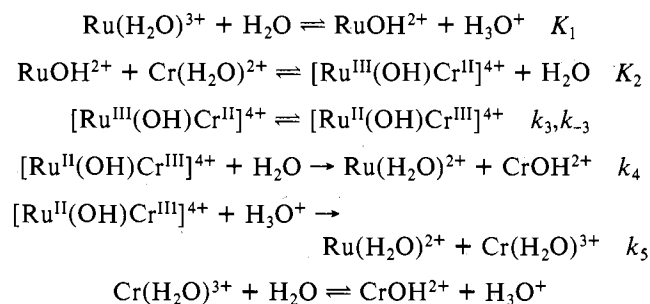$$Ru(H_2O)_6^{3+} + H_2O = Ru(H_2O)_5OH^{2+} + H_3O^+$$

was measured by determining $E_{1/2}$ for the Ru(III)/Ru(II) couple as a function of pH. The results are shown in Figure 1. The measured value of pK_a is 2.90 ± 0.05 at 25 °C with the ionic strength maintained at 1.0 M by using $CF_3SO_3^-$. Evidently the value of K_a for $Ru(H_2O)_6^{3+}$ (1.26 × 10^{-3} M) is similar to the K_a values of trivalent ions of the first transition series.

Discussion

The rates of all of the reactions studied are greater than the rate of water exchange on $Ru(H_2O)_6^{2+}$ ($k \approx 10^{-1}$ s^{-1}) or $Ru(H_2O)_6^{3+}$ ($k \approx 10^{-5}$ s^{-1}).[14] For the most part, they are also faster than water exchange or substitution on the oxidizing or reducing agents, thus excluding the possibility of an inner-sphere mechanism. The reduction of $Ru(H_2O)_6^{3+}$ by $Cr(H_2O)_6^{2+}$ is the only reaction studied that does not proceed by an outer-sphere pathway. By analogy with the reactions of other ruthenium(III) complexes with $Cr(H_2O)_6^{2+}$,[15,18] the intermediate observed in the $Ru(H_2O)_6^{3+}$–$Cr(H_2O)_6^{2+}$ reaction is almost certainly the hydroxo-bridged successor complex. The lack of an acid-independent rate term for the formation of the intermediate indicates that the reaction of unhydrolyzed $Ru(H_2O)_6^{3+}$ and $Cr(H_2O)_6^{2+}$ may be neglected ($k \leq 1 \times 10^3$ M^{-1} s^{-1}). We therefore propose Scheme I in which all of the coordinated water molecules are not shown. In terms of Scheme I, $b/K_1 = K_2k_3$, $k_4 = c = 0.03$ s^{-1}, and $k_5 = d = 1.6$ M^{-1} s^{-1}. In view of the relative labilities of chromium(III) and ruthenium(II), it is likely that the ruthenium–oxygen rather than the chromium–oxygen bond is broken in the dissociation of the successor complex. This conclusion is consistent with the finding that the dissociation of the chloride-bridged successor complex formed in the reaction of $Ru(H_2O)_5Cl^{2+}$ with $Cr(H_2O)_6^{2+}$ produces $Ru(H_2O)_6^{2+}$ and $Cr(H_2O)_5Cl^{2+}$ rather than $Ru(H_2O)_5Cl^+$ and $Cr(H_2O)_6^{3+}$.[15]

Scheme I

$$Ru(H_2O)^{3+} + H_2O \rightleftharpoons RuOH^{2+} + H_3O^+ \quad K_1$$

$$RuOH^{2+} + Cr(H_2O)^{2+} \rightleftharpoons [Ru^{III}(OH)Cr^{II}]^{4+} + H_2O \quad K_2$$

$$[Ru^{III}(OH)Cr^{II}]^{4+} \rightleftharpoons [Ru^{II}(OH)Cr^{III}]^{4+} \quad k_3, k_{-3}$$

$$[Ru^{II}(OH)Cr^{III}]^{4+} + H_2O \rightarrow Ru(H_2O)^{2+} + CrOH^{2+} \quad k_4$$

$$[Ru^{II}(OH)Cr^{III}]^{4+} + H_3O^+ \rightarrow$$
$$Ru(H_2O)^{2+} + Cr(H_2O)^{3+} \quad k_5$$

$$Cr(H_2O)^{3+} + H_2O \rightleftharpoons CrOH^{2+} + H_3O^+$$

The value of K_2k_3 is a factor of 2 larger than the rate constant for the oxidation of $Cr(H_2O)_6^{2+}$ by $Ru(NH_3)_5OH^{2+}$ (3.5 × 10^6 M^{-1} s^{-1}).[22] Although these rate constants are approaching the maximum values observed for inner-sphere oxidation of $Cr(H_2O)_6^{2+}$,[23] the similarity of the rate constants and driving forces for the two hydroxide-bridged reactions suggests similar reorganization parameters for $Ru(H_2O)_5OH^{2+}$ and $Ru(NH_3)_5OH^{2+}$.

The remaining reactions studied proceed by an outer-sphere mechanism, and for these we may calculate an effective (outer-sphere) $Ru(H_2O)_6^{2+}$–$Ru(H_2O)_6^{3+}$ exchange rate constant by using eq 1. The results of these calculations are presented in the last column of Table I. It will be seen that the calculated rate constants are not constant; the values calculated from the very exothermic reactions are lower than those calculated from the reactions with moderate driving
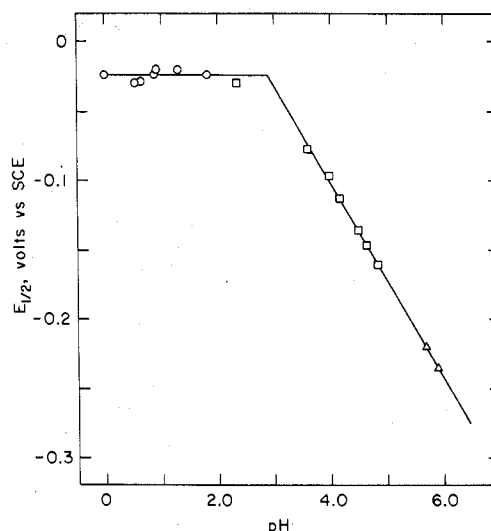

Figure 1. Plot of $E_{1/2}$ vs. pH for the aquoruthenium(III)–aquoruthenium(II) couple at 25 °C and μ = 1.0 M ($LiCF_3SO_3$). The pH was adjusted as follows: circles, CF_3SO_3H; squares, CH_3COO-H–$LiCH_3COO$; triangles, hexamethylenetetramine (($CH_2)_6N_4$).
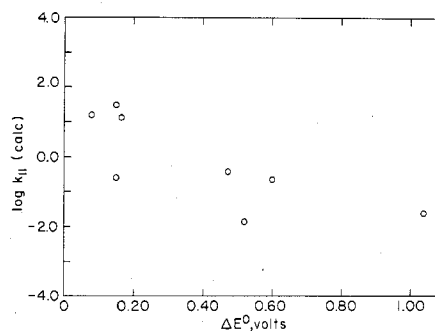
Figure 2. Plot of the logarithm of the calculated rate constant for the $Ru(H_2O)_6^{2+}$–$Ru(H_2O)_6^{3+}$ exchange reaction vs. $\Delta E°$ for the cross reaction. Data are from Table I.

forces. This is not an uncommon finding in the application of eq 1 (eq 1 seldom gives exchange rates that are too high[9]). In view of this complication we have estimated the $Ru(H_2O)_6^{2+,3+}$ exchange rate from the intercept of the plot of the logarithm of the calculated exchange rate constants vs. $\Delta E°$ for the cross reaction (Figure 2).[28] This procedure, which is justified by the results obtained with systems of known exchange rates,[9] gives (6 ± 4) × 10^1 M^{-1} s^{-1} for the rate constant of the $Ru(H_2O)_6^{2+,3+}$ exchange in 1.0 M CF_3SO_3H at 25 °C.

A more direct estimate of the rate constant for the $Ru(H_2O)_6^{2+,3+}$ exchange can, in principle, be obtained from the rate of electron transfer between two ruthenium complexes containing predominantly aquo ligands. The oxidation of $Ru(H_2O)_5Cl^+$ by $Ru(H_2O)_6^{3+}$ (eq 3) was studied for this

$$Ru(H_2O)_5Cl^+ + Ru(H_2O)_6^{3+} \rightarrow$$
$$Ru(H_2O)_5Cl^{2+} + Ru(H_2O)_6^{2+} \quad (3)$$
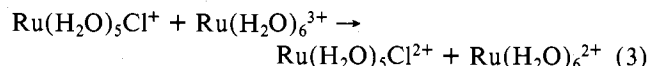
purpose (Table I). The success of this approach requires that the $Ru(H_2O)_6^{2+,3+}$ and $Ru(H_2O)_5Cl^{+,2+}$ couples have similar exchange rates.[24,25] The ratio of the exchange rates of these couples can be obtained from a comparison of the rates of reduction of $Ru(H_2O)_6^{3+}$ and $Ru(H_2O)_5Cl^{2+}$ by a common reducing agent and by using eq 4 to correct for any difference

$$k_{33}/k_{11} = k_{34}^2 K_{14} f_{14}/k_{14}^2 K_{34} f_{34} \quad (4)$$

in the driving forces for the reductions. In this equation k_{11} and k_{33} are the rate constants for the $Ru(H_2O)_6^{2+,3+}$ and the $Ru(H_2O)_5Cl^{+,2+}$ exchange reactions, respectively, k_{34} and K_{34}

are the rate and equilibrium constants for the oxidation of a given reductant by $Ru(H_2O)_5Cl^{2+}$, and k_{14} and K_{14} are the rate and equilibrium constants for the oxidation of the same reductant by $Ru(H_2O)_6^{3+}$. For vanadium(II) as the reductant, the data in Table I give $k_{33}/k_{11} = 1 \times 10^4$. This ratio is 3×10^4 for reduction by $Ru(NH_3)_6^{2+}$. Although the ratios are in satisfactory agreement considering the difference in the driving forces for the reactions, their magnitude vitiates the use of reaction 3 as a model for the $Ru(H_2O)_6^{2+,3+}$ exchange. Evidently replacement of a coordinated water molecule by a chloride (or hydroxide) ion dramatically increases the aquoruthenium(II)–ruthenium(III) exchange rate.[29]

Comparison with Other Systems. The previous discussion has implicated a $Ru(H_2O)_6^{2+,3+}$ exchange rate of $(6 \pm 4) \times 10^1$ M^{-1} s^{-1} (1.0 M CF$_3$SO$_3$H, 25 °C). This rate is surprisingly low: it is only about 10 times larger than the $Fe(H_2O)_6^{2+,3+}$ exchange rate and about 500 times smaller than the rate of the $Ru(NH_3)_6^{2+,3+}$ exchange (Table I). In terms of the model discussed here,[2-11] the relatively slow $Ru(H_2O)_6^{2+,3+}$ exchange rate is evidence either of nonadiabaticity (κ, eq 6, $\simeq 10^{-2}$–10^{-3})

$$k = K_o k_{et} \tag{5}$$

$$k_{et} = \kappa(kT/h) \exp(-\Delta G_\lambda^{\ddagger}/RT) \tag{6}$$

$$\Delta G_\lambda^{\ddagger} = \Delta G_{in}^{\ddagger} + \Delta G_{out}^{\ddagger} \tag{7}$$

or of a significant inner-sphere reorganization barrier ($\Delta G_{in}^{\ddagger}$, eq 7, $\simeq 3$–4 kcal mol^{-1}). The former explanation is not too attractive. According to recent calculations[30] $\kappa \geq 10^{-2}$ for the $Fe(H_2O)_6^{2+,3+}$ exchange, and κ for the reaction of a second-row transition element, with its larger d-orbital extension, is unlikely to be smaller than κ for the exchange reaction of a corresponding first-row couple. Because of this we favor the interpretation that the relatively slow $Ru(H_2O)_6^{2+,3+}$ exchange rate is due to a nonnegligible inner-sphere reorganization barrier.

In the harmonic approximation, the inner-sphere reorganization energy is given by eq 8, where f_2 and f_3 are stretching

$$\Delta G_{in}^{\ddagger} = 3f_2f_3(a_2 - a_3)^2/(f_2 + f_3) \tag{8}$$

force constants and a_2 and a_3 are the M–L bond lengths in the two oxidation states. The relative values of the exchange rate constants suggests that $(a_2 - a_3)$ for the $Ru(H_2O)_6^{2+,3+}$ couple lies between the $(a_2 - a_3)$ values for the $Fe(H_2O)_6^{2+,3+}$ (0.14 Å)[31] and the $Ru(NH_3)_6^{2+,3+}$ (0.04 Å)[32] couples. (The values of K_o and $\Delta G_{out}^{\ddagger}$ are expected to be similar for the $Fe(H_2O)_6^{2+,3+}$, $Ru(H_2O)_6^{2+,3+}$, and $Ru(NH_3)_6^{2+,3+}$ exchanges because of the similar values of $(a_2 + a_3)$ for the three couples.[10]) The large differences between the $Fe(H_2O)_6^{2+,3+}$ and the $Ru(NH_3)_6^{2+,3+}$ $(a_2 - a_3)$ values has been interpreted in terms of ligand field theory as follows.[31] The normally nonbonding metal t_{2g} orbitals become involved in the bonding process if a ligand has empty or filled π orbitals. Water has filled π orbitals which are lower in energy than the metal t_{2g} electrons. The pπ–dπ interactions cause stabilization of the ligand π orbitals, whereas the t_{2g} orbitals become antibonding. Therefore addition or removal of an antibonding t_{2g} electron, as occurs in the $Fe(H_2O)_6^{2+,3+}$ exchange, will be associated with a bond length change. On the other hand, ammonia has no lone pairs available for pπ–dπ interaction. The t_{2g} electrons maintain their nonbonding character, and thus a much smaller inner-sphere reorganization is expected for the $Ru(NH_3)_6^{2+,3+}$ exchange. The $Ru(H_2O)_6^{2+,3+}$ reorganization is expected to be intermediate: the ruthenium centers are low-spin t_{2g}^6 and t_g^5 ions, respectively, and the pπ–dπ interaction is likely to be smaller for this low-spin system than it is in the high-spin $Fe(H_2O)_6^{2+,3+}$ system, where the t_{2g} levels are not completely filled in the reduced ion; on the other hand, the pπ–dπ interaction should be larger in the aquoruthenium system than

it is in the ammine system in which the ligands have no lone pairs.

Entropies of Hydration of the Two Oxidation States. The relative rates of the $Fe(H_2O)_6^{2+,3+}$, $Ru(H_2O)_6^{2+,3+}$, and $Ru(NH_3)_6^{2+,3+}$ exchange reactions can also be discussed in terms of $(S^\circ_{Red} - S^\circ_{Ox})$, the difference in the standard entropies of the two oxidation states of the couples. The value of $(S^\circ_{Red} - S^\circ_{Ox})$ for the $Fe(H_2O)_6^{2+,3+}$, $Ru(H_2O)_6^{2+,3+}$, and $Ru(NH_3)_6^{2+,3+}$ couples are 43 (1 M NaClO$_4$), 38 (0.3 M p-toluenesulfonic acid), and 14 (0.8 M CF$_3$COONa) cal deg^{-1} mol^{-1}, respectively.[33] The exchange rates correlate well with these values; indeed a good straight line is obtained when log k_{ii} is plotted vs. $(S^\circ_{Red} - S^\circ_{Ox})_{ii}$. This linear correlation provides further support for the correctness of the estimate of the $Ru(H_2O)_6^{2+,3+}$ exchange rate. It is not unreasonable to expect that differences in the radii of the two oxidation states will be reflected in the values of $(S^\circ_{Red} - S^\circ_{Ox})$ since the hydration entropies of ions are functions of the radii of the ions as well as of their charges.[34] The generally higher values of $(S^\circ_{Red} - S^\circ_{Ox})$ for hydrated ions compared with the $(S^\circ_{Red} - S^\circ_{Ox})$ values for complexes containing non-hydrogen-bonding ligands can be rationalized in terms of the effective radii of hydrated ions being smaller than the effective radii of complexes that do not contain aquo ligands. Thus in certain models the effective radii of hydrated ions are less than their crystallographic radii.[35,36] By contrast, the effective radii of complexes that do not contain aquo ligands are unlikely to differ much from their crystallographic radii. The importance of hydrogen bonding to the solvent (water) by complexes containing aquo ligands has previously been noted.[22,33] Here we wish to emphasize that differences between the radii of the oxidized and reduced forms of a couple can also lead to substantial $(S^\circ_{Red} - S^\circ_{Ox})$ changes. Indeed differences of 0.1–0.2 Å between the effective radii of the two forms of a 2+,3+ couple can increase $(S^\circ_{Red} - S^\circ_{Ox})$ by 10–20 cal deg^{-1} mol^{-1}.[37] To the extent that bond distance differences between the two oxidation states are reflected in $(S^\circ_{Red} - S^\circ_{Ox})$ differences, some correlation of exchange rates with $(S^\circ_{Red} - S^\circ_{Ox})$ values might be expected. Within this framework the relatively slow exchange rate of the $Ru(H_2O)_6^{2+,3+}$ couple is consistent with its relatively large $(S^\circ_{Red} - S^\circ_{Ox})$ value.

To conclude, application of eq 1 to a number of reactions involving the $Ru(H_2O)_6^{2+,3+}$ couple leads to an estimate of $(6 \pm 4) \times 10^1$ M^{-1} s^{-1} for the $Ru(H_2O)_6^{2+,3+}$ exchange rate. This estimate suggests a fairly large difference (~ 0.1 Å) between the radii of $Ru(H_2O)_6^{2+}$ and $Ru(H_2O)_6^{3+}$ and is consistent with trends in $(S^\circ_{Red} - S^\circ_{Ox})$ for the $Fe(H_2O)_6^{2+,3+}$, $Ru(H_2O)_6^{2+,3+}$, and $Ru(NH_3)_6^{2+,3+}$ couples. A direct determination of the $Ru(H_2O)_6^{2+,3+}$ exchange rate and of the ruthenium–oxygen distances in the two oxidation states would be of considerable interest.

Registry No. $Ru(H_2O)_6^{2+}$, 30251-71-9; $Ru(H_2O)_6^{3+}$, 30251-72-0; $Ru(NH_3)_5$py^{3+}, 33291-25-7; $Ru(NH_3)_5$isn^{3+}, 46372-32-1; Co(phen)$_3^{3+}$, 18581-79-8; Fe(H$_2$O)$_6^{3+}$, 15377-81-8; Os(bpy)$_3^{3+}$, 30032-51-0; Ru(bpy)$_3^{3+}$, 18955-01-6; $Ru(NH_3)_6^{2+}$, 19052-44-9; V(H$_2$O)$_6^{2+}$, 15696-18-1; $Ru(H_2O)_5Cl^+$, 35594-90-2; $Ru(H_2O)_5Cl^{2+}$, 26167-23-7; Cr(H$_2$O)$_6^{2+}$, 20574-26-9.

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(12) Abbreviations used for ligands in this paper are as follows: py, pyridine; isn, isonicotinamide; bpy, 2,2'-bipyridine; phen, 1,10-phenanthroline; terpy, 2,2',2''-terpyridine.
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(25) The values of k_{33}/k_{11} for the reduction of $Ru(NH_3)_5Cl^{2+}$ and $Ru(NH_3)_6^{3+}$ by $V(H_2O)_6^{2+}$ ($k_{34} = 3.0 \times 10^{3 \, 26}$ and $k_{14} = 1.41 \times 10^{3 \, 27}$) is only 3×10^1.
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(29) The $Ru(H_2O)_5Cl^{+,2+}$ and $Ru(NH_3)_5Cl^{+,2+}$ exchange rates calculated in this work are 6×10^5 M^{-1} s^{-1} ($\mu = 1.0$ M) and 1.3×10^5 M^{-1} s^{-1} ($\mu = 0.1$ M), respectively.
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(37) Consistent with this interpretation, it should be noted that $(S^\circ_{\text{Red}} - S^\circ_{\text{Ox}})$ is some 20–25 cal deg^{-1} mol^{-1} more positive for $Co(en)_3^{2+,3+}$, $Co(bpy)_3^{2+,3+}$, and $Co(phen)_3^{2+,3+}$ than for the corresponding ruthenium (and iron) complexes.[32] Based on the electronic configurations of the couples, the values of $(a_2 - a_3)$ are expected to be larger for the cobalt(II)–cobalt(III) than for the corresponding ruthenium(II)–ruthenium(III) or iron(II)–iron(III) couples.

Kinetic Studies of Ring Closures in Platinum(II) Chelates. Rate Constants and Activation Parameters for Chelation of Platinum(II) by Bis(2-aminoethyl) Sulfide in Aqueous Solution

G. ALBERTIN, E. BORDIGNON, A. A. ORIO, B. PAVONI, and HARRY B. GRAY*

The complexes $[PtCl_3(basH_2)]^+$ and $[PtCl_2(basH)]^+$ (bas = bis(2-aminoethyl) sulfide) have been prepared, and the kinetics of Pt–bas ring closures have been studied. In basic media the rate constants for closure of the first and second chelate rings are 3.6 ± 0.2 and 0.173 ± 0.005 s^{-1} ($\mu = 0.4$ M, 25 °C), respectively. Corresponding activation parameters are $\Delta H^\ddagger = 14.2 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = -8.2 \pm 0.8$ cal/(deg mol) (first ring) and $\Delta H^\ddagger = 15.7 \pm 0.1$ kcal/mol and $\Delta S^\ddagger = -9.0 \pm 0.5$ cal/(deg mol) (second ring). The results when compared with data obtained for ring closures in tridentate nitrogen-donor Pt(II) chelates suggest that ring strain is involved in reaching the transition states, with the second closure involving more strain than the first.

Introduction

Four-coordinate, planar complexes of platinum(II) containing polydentate amine ligands have been studied extensively.[1] Very little is known, however, about the activation energetics associated with closure of the two rings in the formation of a tridentate chelate of Pt(II). For this reason, we have synthesized the complexes $[PtCl_3(basH_2)]^+$ and $[PtCl_2(basH)]^+$ (bas = bis(2-aminoethyl) sulfide) and have investigated the kinetics of the ring-closure reactions. This study has allowed a comparison of the kinetic data with similar results previously reported on the closure of the first[2] and of the second rings[2,3] in *trans*-$[PtCl_2(enH)_2]^{2+}$ (enH = monoprotonated ethylenediamine) and $[PtCl_2(bama)\cdot HCl]$ (bama = bis(2-aminoethyl)methylamine). Information on the influence of the nature of the central atom of the bas ligand on the ring-closure rates has thus been obtained.

Experimental Section

Materials. Commercial reagent grade chemicals were used without further purification. K_2PtCl_4 was obtained from Johnson-Matthey and bis(2-aminoethyl) sulfide(bas) was prepared by the method of Smolin and co-workers[4] or by the alkaline hydrolysis of diphthalimidodiethyl sulfide.[5]

*To whom correspondence should be addressed at California Institute of Technology.

Measurements. Conductivities of 10^{-3} M solutions of Pt(II) complexes in dimethyl sulfoxide or water were measured at 25 °C by using a Halosis bridge. Infrared spectra of KBr pellets and Nujol mulls were recorded on a Perkin-Elmer 457 spectrophotometer.

Synthesis of Complexes. [Bis(2-aminoethyl) sulfide)]trichloroplatinum(II) Chloride, $[PtCl_3(basH_2)]Cl$. To a stirred solution of 1.2 g (10 mmol) of $S(CH_2CH_2NH_2)_2$ in 50 mL of 2 M HCl at room temperature was added at ca. 0.2 mL/min an aqueous solution (50 mL) of 4.15 g (10 mmol) of K_2PtCl_4. The resulting orange solution was concentrated to 20–25 mL and cooled at 5 °C. The KCl precipitated at this stage was removed by suction filtration. By further concentration of the solution, orange crystals of $[PtCl_3(basH_2)]Cl$ were obtained. These were recrystallized from 2 M HCl. The yield was ca. 60%. Anal. Calcd: C, 10.46; H, 3.07; N, 6.10; Cl, 30.88. Found: C, 10.10; H, 3.14; N, 5.80; Cl, 30.39. Mp (uncor) 222 °C.

[Bis(2-aminoethyl) sulfide hydrochloride]dichloroplatinum(II), $[PtCl_2(bas\cdot HCl)]$. This complex was obtained under the same experimental conditions as in the previous preparation, except that the pH was kept in the range 1–2. The resulting yellow-orange solution was concentrated to 20–25 mL and cooled, whereupon white crystals of KCl separated out. The $[PtCl_3(basH_2)]Cl$ and $[PtCl_2(bas\cdot HCl)]$ complexes, which are both present in the final solution, were separated by fractional crystallization. The yellow compound $[PtCl_2(bas\cdot HCl)]$, which was precipitated initially, was recrystallized from 1 M HCl (5 mL) (yield 40%). These complexes were also prepared in a different way by Mann[6] but were not characterized completely. Anal. Calcd: C, 11.37; H, 3.10; N, 6.63; Cl, 25.16. Found: C, 11.06; H, 3.42; N,