The Reaction of Chloropentaaquoruthenium(III) with Chromium(II). Binuclear Intermediates, Reduction of Perchlorate, and the Effect of Vanadium(II)[1]

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Abstract: The reaction of chromium(II) with chloropentaaquoruthenium(III) in perchloric acid solution produces a chloride-bridged chromium(III)–ruthenium(II) intermediate. In the range ($HClO_4$) = 1.0 to 0.20 *M* the rate constant for the dissociation of the intermediate is given by $k_{obsd} = a + b/(H^+)$ where $a = 1.20 \pm 0.06$ sec^{-1} and $b = 0.36 \pm 0.03$ *M* sec^{-1} at 25.0°. The dissociation of the intermediate produces Cr^{3+} and $CrCl^{2+}$; the yield of $CrCl^{2+}$ is 88 ± 5% in 1.0 *M* perchloric acid and decreases with decreasing acidity. Vanadium(II) catalyzes the disappearance of the intermediate. The rate constant for the reaction of vanadium(II) with chloropentaaquoruthenium(III) is $(1.88 \pm 0.06) \times 10^3$ M^{-1} sec^{-1} at 25.0° and is independent of acidity in the range ($HClO_4$) = 1.0 to 0.10 *M*. The reaction of chromium(II) with perchlorate ion is catalyzed by ruthenium(II). The rate law for this reaction is $d(CrCl^{2+})/dt = k[Ru(II)][ClO_4^-]$ where $k = (3.3 \pm 0.3) \times 10^{-3}$ M^{-1} sec^{-1} at 25.0° and 1.0 *M* ionic strength. The mechanisms of these reactions are discussed.

Inner-sphere mechanisms have been established for many electron-transfer reactions. However, only in very few cases have the binuclear intermediates formed in these reactions been observed directly.[2,3] The presence of these intermediates is usually inferred from rate comparisons, from the rate law, or from the identities of the products of the electron-transfer reaction. This paper is concerned with the binuclear intermediates formed in the reaction of chloropentaaquoruthenium(III) with chromium(II). This system was chosen for study because of the relatively stable d^6 and d^3 electron configurations of the products. The reaction of chloropentaaquoruthenium(III) with vanadium(II) and some of the properties of perchloric acid solutions containing ruthenium(II) and chromium(II) are also described.

Experimental Section

Materials. Solutions containing chloropentaaquoruthenium(III) were prepared by refluxing a solution of 1.5 g of ruthenium trichloride in 50 ml of 0.1 *M* hydrochloric acid over 40 ml of mercury at 75° for 6 hr. The resulting dark brown solution was filtered and then stirred for 2 days with about 30 g of Dowex 50W-X12 ion-exchange resin (200–400 mesh) in the H^+ form. The equilibrated resin was placed in a column of 1 in. diameter on top of about 2 in. of resin which had not been treated with the ruthenium(III). A mixture of $RuCl_3$ and $RuCl_2^+$ was eluted with 0.1 *M* perchloric acid and the $RuCl^{2+}$ was eluted with 1.0 *M* perchloric acid.[4,5] The eluate containing $RuCl^{2+}$ was subjected to an additional purification step by diluting it tenfold with water, passing it through an ion-exchange column in the H^+ form, and eluting the $RuCl^{2+}$ with 1.0 *M* perchloric acid. The $RuCl^{2+}$ concentration was determined spectrophotometrically using ϵ 670 at 317 nm. Total ruthenium was determined according to the procedure described by Ayres and Young.[6] The ruthenium concentration determined by the two methods generally agreed to within 5%. Total chloride was determined as silver chloride by heating a solution of $RuCl^{2+}$ with Ag^+. The chloride determined in this procedure was about 12% higher than the amount calculated from the ruthenium(III) concentrations of the solutions. The additional chloride was formed in the oxidation of ruthenium(III) by perchlorate during the analytical procedure.

Solutions of $RuCl^{2+}$ gradually decompose upon standing at room temperature. The rate of decomposition increases with the $RuCl^{2+}$ and perchloric acid concentrations of the solutions. The $RuCl^{2+}$ was therefore used as soon as possible after preparation. That fraction which was not used immediately was diluted tenfold with water, stored at 5°, and purified by adsorption and elution from the ion-exchange column before use.

Solutions containing chromium(II) or vanadium(II) were prepared by reducing chromium(III) or vanadium(IV) with amalgamated zinc immediately before use. Chromium(II)–vanadium(II) mixtures were prepared by adding chromium(II) to the vanadium(II) solutions. Other reagents were prepared and standardized as previously described.[7]

Procedure. The oxidation–reduction reactions were studied by the use of the flow apparatus which is described elsewhere.[8] The disappearance of the intermediates was followed at 410 nm where the absorbance change was maximal. The following concentration ranges were used: (Cr^{2+}) = 8.0×10^{-3} to 4.0×10^{-2} *M*; ($RuCl^{2+}$) = 1.33×10^{-4} to 7.15×10^{-4} *M*; and ($HClO_4$) = 0.1 to 1.0 *M*, and ionic strength 1.0 *M*. The rate constants were obtained from slopes of plots of log $(D_t - D_\infty)$ *vs.* time, where D_t and D_∞ are the optical densities at time *t* and at the end of the reaction, respectively. All of the kinetic measurements were made at 25.0°.

The yield of $CrCl^{2+}$ in the $RuCl^{2+}$–Cr^{2+} reaction was determined by flowing the reaction mixture through a 92-cm long polythene tube (i.d. = 3.9 mm) into a conical flask containing sufficient sodium persulfate to react with the excess chromium(II). The quenched solution was diluted fivefold and placed on a Dowex 50W-X8 ion-exchange column. The column was washed with 0.2 *M* perchloric acid and the $CrCl^{2+}$ was eluted with 1 *M* perchloric acid. Total chromium in the eluate was determined by the diphenylcarbazide method[9] and in some instances also as chromate (ϵ 4.83 $\times 10^3$ at 372 nm) after oxidation with alkaline peroxide. The rate of formation of $CrCl^{2+}$ in the ruthenium(II)-catalyzed reduction of perchlorate by chromium(II) was studied by flowing the $RuCl^{2+}$–Cr^{2+} reaction mixture into 25-ml volumetric flasks in an argon atmosphere. At varying intervals excess sodium persulfate was added to the flasks to quench the reaction and the $CrCl^{2+}$ determined as described above. In later experiments the reaction mixture was flowed under argon into a 10-cm cell and the formation of chromium(III) followed at 410 nm, using ϵ 130 for the formation of $CrCl^{2+}$ ($\epsilon_{CrCl^{2+}} + 7\epsilon_{Cr^{3+}}$). The perchlorate ion concentration of the

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[2] H. Taube, Award Address, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[3] N. Sutin, *Ann. Rev. Phys. Chem.*, 17, 119 (1966).

[4] H. H. Cady, Ph.D. Thesis, University of California, 1957.

[5] H. H. Cady and R. E. Connick, *J. Amer. Chem. Soc.*, 80, 2646 (1958).

[6] G. H. Ayres and F. Young, *Anal. Chem.*, 22, 1281 (1950).

[7] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, 88, 434 (1966).

[8] G. Dulz and N. Sutin, *Inorg. Chem.*, 2, 917 (1963).

[9] B. E. Saltzman, *Anal. Chem.*, 24, 1016 (1952).

solutions was varied by maintaining the ionic strength with *p*-toluenesulfonic acid (HPTS).

Results and Discussion

Chromium(II)–Chloropentaaquoruthenium(III) Reaction. The reaction between chromium(II) and chloropentaaquoruthenium(III) proceeds in two stages. The first stage proceeds too rapidly to be followed on the flow apparatus ($k \geqslant 2 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ in 1.0 *M* perchloric acid at 25.0°); the second stage, however, can readily be followed at 410 nm. The kinetic data are summarized in Table I. The first-order rate constants calculated from the absorbance changes at 410 nm are independent of the chromium(II) and ruthenium(III) concentrations of the solutions provided $(\text{Cr}^{2+})_0/(\text{RuCl}^{2+})_0 \geqslant 20$, and increase with decreasing acidity. In the range $(\text{HClO}_4) = 1.0$ to $0.20\ M$[10] the observed rate constant is given by

$$k_{\text{obsd}} = a + \frac{b}{(\text{H}^+)} \qquad (1)$$

where $a = 1.20 \pm 0.06\ \text{sec}^{-1}$ and $b = 0.36 \pm 0.03\ M\ \text{sec}^{-1}$ at 25.0°. It is also apparent from Table I that the value of $\Delta\text{Abs}/l(\text{RuCl}^{2+})_0$ at 410 nm, where ΔAbs is the total change in the absorbance accompanying the decay of the intermediate and *l* is the diameter of the observation tube, is independent of the initial concentration of RuCl^{2+} and also of the acidity provided the latter is greater than about 0.2 *M*.

Table I. First-Order Rate Constants for the Disappearance of the Intermediate Produced in the Chromium(II)–Chloropentaaquoruthenium(III) Reaction at 25.0°

(HClO_4), *M*	$(\text{Cr}^{2+})_0 \times 10^3$, *M*	$(\text{RuCl}^{2+})_0 \times 10^4$, *M*	*k*, sec^{-1}	$\dfrac{\Delta\text{Abs}^a}{l(\text{RuCl}^{2+})_0}$
1.00	40.0	5.30	1.57	1.23
1.00	25.9	5.30	1.44	1.18
1.00	24.0	3.60	1.60	1.22
1.00	24.0	1.60	1.52	1.12
1.00	15.6	5.30	1.49	1.17
1.00	8.0	2.85	1.53	1.20
1.00	8.0	1.33	1.47	1.21
0.91	24.0	2.45	1.58	1.15
0.85	15.6	2.65	1.60	1.20
0.75	15.6	5.30	1.59	1.26
0.75	24.0	3.60	1.81	1.17
0.70	24.0	2.45	1.75	1.16
0.60	24.0	2.45	1.73	1.04
0.60	15.6	2.65	1.78	1.23
0.60	24.0	3.60	1.93	1.18
0.50	24.0	2.80	2.00	1.17
0.50	15.6	5.30	1.98	1.18
0.49	40.0	2.50	1.97	1.20
0.44	24.0	7.15	2.13	1.17
0.40	40.0	2.50	2.04	1.22
0.40	15.6	2.60	2.04	1.22
0.34	40.0	2.70	1.97	1.11
0.34	40.0	2.50	2.13	1.15
0.30	15.6	5.30	2.36	1.21
0.30	24.0	2.80	2.46	1.17
0.29	24.0	7.15	2.53	1.11
0.26	15.6	5.30	2.46	1.20
0.26	40.0	2.50	2.26	1.07
0.25	24.0	2.80	2,67	1.12
0.24	24.0	7.15	2.66	1.19
0.20	24.0	3.65	2.86	1.15
0.19	15.6	5.30	2.81	1.19
0.15	24.0	3.65	3.30	1.10

[a] ΔAbs is the total change in absorbance accompanying the decay of the intermediate at 410 nm, and *l* is the path length of the observation tube (1.9 mm).

Both Cr^{3+} and CrCl^{2+} are produced in the reaction between chromium(II) and chloropentaaquoruthenium(III). The yield of CrCl^{2+} is 88 ± 5% in 1.0 *M* perchloric acid, approaches 100% as $1/(\text{HClO}_4)$ tends to zero, and decreases with decreasing acidity. In the range $(\text{HClO}_4) = 1.0$ to $0.20\ M$ the yield of CrCl^{2+}, *i.e.*, the ratio of $(\text{CrCl}^{2+})/[\text{Cr(III)}]$ produced in the reaction, is given by

$$\frac{(\text{CrCl}^{2+})}{(\text{RuCl}^{2+})_0} = \frac{c + d/(\text{H}^+)}{k_{\text{obsd}}} \qquad (2)$$

with $c = 1.21 \pm 0.03\ \text{sec}^{-1}$ and $d = 0.09 \pm 0.01\ M\ \text{sec}^{-1}$ at 25.0°. Although the kinetic measurements do not establish the composition or the structure of the intermediate, the stoichiometric data indicate that the intermediate formed at the higher acidities is $[\text{Ru}^{\text{II}}\text{ClCr}^{\text{III}}]^{4+}$. This result is not unexpected for neither ruthenium(II) nor chromium(III) undergoes substitution readily. The kinetic data are consistent with the following scheme.

$$\text{RuCl}^{2+} + \text{Cr}^{2+} \xrightarrow{\text{rapid}} [\text{Ru}^{\text{II}}\text{ClCr}^{\text{III}}]^{4+} \qquad (3)$$

$$[\text{Ru}^{\text{II}}\text{ClCr}^{\text{III}}]^{4+} \xrightarrow{k_1} \text{Ru}^{2+} + \text{CrCl}^{2+} \qquad (4)$$

The increase in the rate of dissociation of the intermediate with decreasing acidity suggests a contribution from

$$[\text{Ru}^{\text{II}}\text{ClCr}^{\text{III}}]^{4+} + \text{H}_2\text{O} \rightleftharpoons [\text{Ru}^{\text{II}}\text{ClCr}^{\text{III}}\text{OH}]^{3+} + \text{H}^+ \quad K_\text{h} \qquad (5)$$

$$[\text{Ru}^{\text{II}}\text{ClCr}^{\text{III}}\text{OH}]^{3+} \begin{array}{l} \xrightarrow{k_a} \text{Ru}^{2+} + \text{Cr(OH)Cl}^+ \qquad (6\text{a}) \\ \xrightarrow{k_b} \text{RuCl}^+ + \text{CrOH}^{2+} \qquad (6\text{b}) \end{array}$$

reactions 5 and 6. Reactions 3, 4, 5, and 6 can account for the principal features of the kinetic and stoichiometric results.[11] In terms of the above scheme, $a = c = k_1$, $b = K_hk_2$, $d = K_hk_a$, with $k_2 = (k_a + k_b)$.[12] It will be seen that the experimental values of *a* and *c* are in good agreement. Comparison of the values of *b* and *d* gives $k_b/k_a = 3$. Evidently the ruthenium–chloride bond breaks at least 20 times more frequently than the chromium–chloride bond in $[\text{RuClCr}]^{4+}$. In $[\text{RuClCrOH}]^{3+}$, on the other hand, the chromium–chloride bond breaks about three times more frequently than the ruthenium–chloride bond. Presumably the chromium–chloride bond is labilized by the hydroxide group which is attached to the chromium, an effect which has also been observed in other systems. These systems are compared in Table II. The mercury(II)-catalyzed aquations are included in this table, for the rates of these reactions are much less rapid than the rate of substitu-

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[10] The first-order plots become curved (and wavelength dependent) at acidities below about 0.2 *M*. This curvature and wavelength dependence could be due to the formation of increasing amounts of a hydroxide-bridged species as the acidity is lowered.

[11] Since chromium(III) is probably more highly hydrolyzed than ruthenium(II), it is likely that the hydroxide group is attached to the chromium(III) in the hydrolyzed form of the intermediate.

[12] This interpretation assumes that $K_h/(\text{H}^+) \ll 1$. This assumption is consistent with the observation that the absorbance change at 410 nm is independent of acidity in the range $(\text{HClO}_4) = 1.0$ to $0.2\ M$. This observation indicates, but does not prove, that the intermediate exists predominantly in a single, acid-independent form.

Table II. Comparison of Rate Constants for the Acid-Independent and Inverse-Acid Paths for the Aquation of Monochlorochromium(III) Complexes at 25.0°, $RClCr^{n+} \rightarrow RCl^{(n-3)} + Cr^{3+}$

Rate law term	Rate constant	k_0/k_{-1}, M^{-1}	Ref
$k_0(CrCl^{2+})$	2.77×10^{-7} sec^{-1}		
$k_{-1}(CrCl^{2+})/(H^+)$	2.84×10^{-8} M sec^{-1}	9.8	*b*
$k_0(RuClCr^{4+})$	$\leqslant 6.0 \times 10^{-2}$ sec^{-1}		
$k_{-1}(RuClCr^{4+})/(H^+)$	2.7×10^{-1} M sec^{-1} [a]	$\leqslant 0.2$	*c*
$k_0(CrCl^{2+})(Hg^{2+})$	4.78×10^{-2} M^{-1} sec^{-1}		
$k_{-1}(CrCl^{2+})(Hg^{2+})/(H^+)$	2.66×10^{-2} sec^{-1}	1.8	*d*
$k_0(CrCl^{2+})(HgCl^+)$	1.05×10^{-1} M^{-1} sec^{-1}		
$k_{-1}(CrCl^{2+})(HgCl^+)/(H^+)$	4.70×10^{-2} sec^{-1}	2.2	*d*

[a] Rate constant for the rupture of the chromium–chloride bond (K_hk_b); the rate constant for the rupture of the ruthenium–chloride bond is not included. [b] T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965). [c] This work. [d] J. H. Espenson and J. P. Birk, *Inorg. Chem.*, **4**, 527 (1965).

tion on mercury(II). This indicates that the mercury-catalyzed reactions proceed through chloride-bridged

$$Hg^{2+} + CrCl^{2+} \rightleftharpoons [HgClCr]^{4+} \quad (7)$$

$$[HgClCr]^{4+} \longrightarrow HgCl^+ + Cr^{3+} \quad (8)$$

intermediates.[13,14] The equilibrium constant for the formation of the chloride-bridged intermediate cancels in the ratio k_0/k_{-1}. It is apparent from Table II that the value of k_0/k_{-1} is smallest for the ruthenium complex, indicating perhaps an enhanced sensitivity of the chromium–chloride bond in this complex to the labilizing effect of a hydroxide group attached to the chromium(III).[15]

Finally, although transfer of the bridging group generally occurs in inner-sphere reactions, reaction 6 is an example of an inner-sphere reaction in which transfer of the bridging group does not occur quantitatively. Early experiments[16] indicated that the inner-sphere reaction of $IrCl_6^{2-}$ with chromium(II) was another example of nonquantitative transfer of the bridging group for it was found that Cr^{3+}, rather than $CrCl^{2+}$, was produced in the reaction. However, this conclusion has recently been questioned.[17] The recent studies show that both Cr^{3+} and $CrCl^{2+}$ are produced in the reaction of $IrCl_6^{2-}$ with Cr^{2+}, but that the yield of Cr^{3+} does not increase with decreasing acidity. It was argued[17] that an increase in the yield of Cr^{3+} should have occurred when the acidity was lowered if the dissociation of $[Cl_5IrClCr]$ produced Cr^{3+}, since lowering the acidity should have labilized the chromium–chloride bond. This labilization is observed, for example, in the aquation of $[RuClCr]^{4+}$ as has been discussed above. It was therefore concluded that the reaction of $IrCl_6^{2-}$ with Cr^{2+} proceeds *via* parallel inner- and outer-sphere paths, and that Cr^{3+} is formed predominantly in the outer-sphere path, while transfer of the bridging chloride group to form $CrCl^{2+}$ occurs in the inner-sphere path. It may be noted that there is no evidence for an outer-sphere path in the reaction of $RuCl^{2+}$ with Cr^{2+} since $CrCl^{2+}$ is the sole product of the acid-independent reaction in this system.

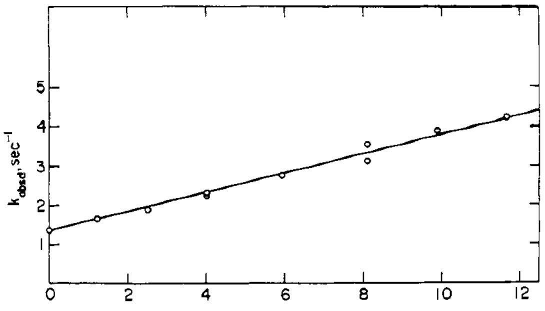

Figure 1. Plot of k_{obsd} *vs.* $(V^{2+})/(Cr^{2+})$ at 25.0°; $(HClO_4) = 1.0$ M.

The Vanadium(II)–Chloropentaaquoruthenium(III) Reaction. The reaction between vanadium(II) and chloropentaaquoruthenium(III) can readily be followed at 317 nm, the absorbance maximum of $RuCl^{2+}$. The rate constant for this reaction is $(1.88 \pm 0.06) \times 10^3$ M^{-1} sec^{-1} at 25.0° and is independent of acidity in the range $(HClO_4) = 1.0$ to 0.1 M. The oxidation–reduc-

$$RuCl^{2+} + V^{2+} \longrightarrow RuCl^+ + V^{3+} \quad (9)$$

tion reaction must proceed by an outer-sphere mechanism, for the rate of the reaction is faster than the rate of substitution on vanadium(II).[18]

An attempt was made to determine the rate of reaction of $RuCl^{2+}$ with Cr^{2+} by mixing a solution containing $RuCl^{2+}$ with one containing both chromium(II) and vanadium(II). Although this type of competition experiment proved unsuccessful (the added vanadium(II) did not decrease the amount of $[Ru^{II}ClCr^{III}]^{4+}$ produced), it was found that the rate constant for the disappearance of $[Ru^{II}ClCr^{III}]^{4+}$ (as determined from the rate of change of absorbance at 410 nm) increased with increasing $(V^{2+})/(Cr^{2+})$. The kinetic data are plotted in Figure 1. It is apparent from this figure that k_{obsd} is linearly related to $(V^{2+})/(Cr^{2+})$; the slope of the straight line is 0.24 ± 0.01 sec^{-1}. The yield of $CrCl^{2+}$ also decreases as the ratio $(V^{2+})/(Cr^{2+})$ increases. The effect of added vanadium(II) in the rate of disappearance of the intermediate can be rationalized in terms of the equilibrium

$$[Ru^{II}ClCr^{III}]^{4+} \rightleftharpoons RuCl^{2+} + Cr^{2+} \quad K_4 \quad (10)$$

followed by reaction 9. In terms of this scheme the slope of the plot of k_{obsd} *vs.* $(V^{2+})/(Cr^{2+})$ is equal to K_4k_4 where k_4 is the rate constant for reaction 9. Substitution of $k_4 = 1.88 \times 10^3$ M^{-1} sec^{-1} gives $K_4 = 1.3 \times 10^{-4}$ M at 25.0°. Although an independent determination of K_4 is not available for comparison, this value of K_4 seems quite reasonable. It should also be noted that the value of K_4^{-1} estimated in this manner is sufficiently large so that the reaction between $RuCl^{2+}$ and Cr^{2+} to form $[Ru^{II}ClCr^{III}]^{4+}$ goes essentially to completion at the chromium(II) concentrations used in this work.[19]

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(13) Analogous anion-bridged intermediates obtain in the mercury(II)-catalyzed aquation of chromium(III)–thiocyanate complexes: A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 434 (1966), and ref 14.

(14) M. Orhanovic and N. Sutin, *ibid.*, **90**, 4286 (1968).

(15) It should be remembered that k_{-1} is a composite constant and includes K_h, the hydrolysis constant of the bridged intermediate.

(16) H. Taube and H. Myers, *J. Amer. Chem. Soc.*, **76**, 2103 (1954).

(17) R. N. F. Thorneley and A. G. Sykes, *Chem. Commun.*, 331 (1969).

(18) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

(19) The complete expression for the observed rate constant for the reaction between chromium(II) and chloropentaaquoruthenium(III) is

$$k_{\mathrm{obsd}} = k_1K_4^{-1}[\mathrm{Cr(II)}]/(1 + K_4^{-1}[\mathrm{Cr(II)}])$$

Since $K_4^{-1}[\mathrm{Cr(II)}] \gg 1$ it follows that $k_{\mathrm{obsd}} = k_1$ under the conditions used in these studies.

The vanadium(II)-catalyzed disappearance of $[Ru^{II}ClCr^{III}]^{4+}$ is a rather novel type of reaction. The added vanadium(II) reacts with the $RuCl^{2+}$ existing in equilibrium with the $[Ru^{II}ClCr^{III}]^{4+}$ thereby promoting the dissociation of the binuclear species into reactants at the expense of its "normal" dissociation into products. In other words, although initially the vanadium(II) fails to react with a significant amount of $RuCl^{2+}$ because of the more rapid reaction of the latter with chromium(II), an appreciable fraction of the $RuCl^{2+}$ is nevertheless consumed by the vanadium(II) in the over-all reaction as a consequence of the relatively slow dissociation of $[Ru^{II}ClCr^{III}]^{4+}$ into products.

The Individual Steps. Although the formation of $[Ru^{II}ClCr^{III}]^{4+}$ from $RuCl^{2+}$ and chromium(II) has been referred to as the first stage in the over-all reaction, this stage proceeds in two steps with $k_sk_e/k_{-s}k_{-e}$ =

$$RuCl^{2+} + Cr^{2+} \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} [Ru^{III}ClCr^{II}]^{4+} \qquad (11)$$

$$[Ru^{III}ClCr^{II}]^{4+} \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} [Ru^{II}ClCr^{III}]^{4+} \qquad (12)$$

$1/K_4$. The first step involves substitution on chromium(II), while the electron transfer from chromium(II) to ruthenium(III) occurs in the second step. The value of k_s is probably about 3×10^7 M^{-1} sec^{-1}, since this is the rate constant observed for substitution on chromium(II) in other oxidation–reduction reactions.[14] Moreover the kinetic data give $k_sk_e/k_{-s} \geqslant 2 \times 10^4$ M^{-1} sec^{-1}; consequently $k_e/k_{-s} \geqslant 6.6 \times 10^{-4}$ and $k_{-e} \geqslant$ 2.6 sec^{-1}. This estimate of the lower limit of k_{-e} is consistent with the mechanism proposed for the vanadium(II) effect for it shows that the dissociation of $[Ru^{II}ClCr^{III}]^{4+}$ into reactants can compete with its dissociation into products under suitable conditions.

The reduction potentials of the couples $Ru(H_2O)_6^{3+} + e = Ru(H_2O)_6^{2+}$ and $RuCl_2^+ + e = RuCl_2$ are 0.2342 ± 0.0088 and 0.01 ± 0.03 V, respectively, in p-toluenesulfonic acid at 25°.[20] If it is assumed that the reduction potential of the $RuCl^{2+}|RuCl^+$ couple is 0.05 V, and that the stability constant of $RuCl^+$ is similar to that of $CrCl^{2+}$ (1.1×10^{-1} M^{-1} at 25°),[21] then the equilibrium constant of the over-all reaction

$$RuCl^{2+} + Cr^{2+} \rightleftharpoons Ru^{2+} + CrCl^{2+} \qquad (13)$$

is calculated to be 5×10^7. This value together with $K_4 = 1.3 \times 10^{-4}$ M gives 7×10^3 M for the equilibrium constant of the reaction

$$[Ru^{II}ClCr^{III}]^{4+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru^{2+} + CrCl^{2+}$$

Since $k_1 = 1.20$ sec^{-1}, the value of k_{-1} is calculated to be 2×10^{-4} M^{-1} sec^{-1}. Finally, comparison of k_{-1} with k_s indicates that ruthenium(II) is about 10^{11} times more substitution inert than chromium(II), or, put somewhat differently, the average lifetime of a water molecule in the inner coordination sphere of ruthenium(II) is estimated to be several minutes at 25°. This estimate is consistent with some qualitative observations on the rate of substitution reactions involving the $Ru(H_2O)_6^{2+}$ ion.[22]

The Chromium(II)–Perchlorate Reaction. The decay of the intermediates produced in the reaction between chromium(II) and chloropentaaquoruthenium(III) is followed by a slower reaction producing $CrCl^{2+}$. The yield of $CrCl^{2+}$, *i.e.*, the ratio $(CrCl^{2+})/Cr(III)$ produced in this reaction, is 12.5 ± 1.0%. This stoichiometry conforms closely to that expected for the oxidation of chromium(II) by perchlorate ions. In the presence of

$$8Cr(II) + ClO_4^- + 8H^+ \longrightarrow CrCl^{2+} + 7Cr(III) + 4H_2O$$

excess chromium(II) the initial rate of formation of $CrCl^{2+}$ is given by

$$d(CrCl^{2+})/dt = k_3[Ru(II)][ClO_4^-] \qquad (14)$$

where $k_3 = (3.3 \pm 0.3) \times 10^{-3}$ M^{-1} sec^{-1} at 25.0° and ionic strength 1.0 M. The kinetic data are summarized in Table III. The rate is independent of acidity in the range $(HClO_4)$ = 0.15 to 1.0 M and is constant for the first 50% of the reaction after which it gradually decreases.[23] The kinetic data are consistent with a rate-determining step involving the reaction of perchlorate with ruthenium(II) followed by the rapid reaction of chromium(II) with the oxidized ruthenium and with chlorate ions. The second-order rate constant for the

$$Ru(II) + ClO_4^- \longrightarrow Ru(IV) + ClO_3^-$$

$$ClO_3^- + 6Cr^{2+} \longrightarrow CrCl^{2+} + 5Cr^{3+}$$

$$Ru(IV) + 2Cr^{2+} \longrightarrow Ru(II) + 2Cr^{3+}$$

Ru^{2+}–ClO_4^- reaction at 25.0° (3.3×10^{-3} M^{-1} sec^{-1}) may be compared with 3.0×10^{-4} M^{-1} sec^{-1} for the $Ru(NH_3)_6^{2+}$–ClO_4^- reaction (μ 0.62 M), and 1.6×10^{-2} M^{-1} sec^{-1} for the $Ru(NH_3)_5^{2+}$–ClO_4^- reaction (μ 0.2 M).[24] It has been proposed that the rate-determining step in the latter reactions involves the transfer of an oxygen atom from perchlorate to ruthenium(II),[24] and it is very likely that a similar mechanism obtains also in the aquo system.

Table III. Second-Order Rate Constant for the Formation of $CrCl^{2+}$in the Ruthenium(II)-Catalyzed Reaction between Chromium(II) and Perchlorate Ions in 1.0 M Perchloric Acid at 25.0°

$(Cr^{2+})_0 \times 10^3$, M	$(RuCl^{2+})_0 \times 10^5$, M	$k \times 10^3$, M^{-1} sec^{-1}
50.0[a]	35.1	3.3
10.5	1.22	3.0
10.5	2.60	3.3
10.5	5.66	3.3
10.5	10.4	3.5
10.5	31.2	3.8
27.0	5.65	3.4
8.50[b]	16.5	3.5
20.5[c]	25.4	3.6
20.5[d]	25.4	3.8

[a] Reaction quenched by the addition of persulfate. The $CrCl^{2+}$ was determined after separation by ion exchange. [b] $(HClO_4)$ = 0.15 M; $(NaClO_4)$ = 0.86 M. [c] $(HClO_4)$ = 0.50 M; (HPTS) = 0.50 M. [d] $(HClO_4)$ = 0.20 M; (HPTS) = 0.80 M.

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

[21] R. J. Baltisberger and E. L. King, *J. Amer. Chem. Soc.*, **86**, 795 (1964).

[22] E. E. Mercer and R. R. Buckley, *Inorg. Chem.*, 4, 1692 (1965).

[23] This decrease in rate could be due to the formation of ruthenium(III) species which are not rapidly reduced by chromium(II). For example, reactions such as $Ru(IV) + Ru(II) \rightarrow [Ru(III)]_2$ could become increasingly important as the chromium(II) concentration decreased, and could account for the rate decrease if the reaction between $[Ru(III)]_2$ and chromium(II) is relatively slow.

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