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Studies on Oxidation–Reduction Reactions of Ruthenium Ammines

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Kinetic and stoichiometric measurements of the reductions of $Ru(NH_3)_6^{+3}$ by $Cr^{+2}(aq)$ (Cl^- independent as well as Cl^- catalyzed paths) and stoichiometries of the reaction of $Ru(NH_3)_5Cl^{+2}$ with Cr^{+2} are reported. Evidence is presented that the reduced species is in each case a Ru(II) ammine and that the ammine ligands remain in the Ru(II) coordination sphere for reasonable periods of time. The standard oxidation potential of $Ru(NH_3)_6^{+2} = Ru(NH_3)_6^{+3} + e^-$ has been determined as −0.214 v. Further kinetic studies of oxidation of Ru(II) species by ClO_4^- and Co(III) ammines are reported. Equilibrium quotients for the anation of $Ru(NH_3)_5OH_2^{+3}$ by Cl^-, Br^-, and I^- have been determined taking advantage of the catalysis of the reactions by $Ru(NH_3)_5OH_2^{+2}$.

The results obtained in preliminary investigations of the complex ammines of Ru(II) have been described in the literature.[1,2] In our present work we have in the main confirmed the earlier results and have considerably extended the investigation of Ru(II) ammine complexes. We find that the pentaammine and hexaammine Ru(II) species are tractable in aqueous solution, although they do decompose slowly and by reactions which are by no means fully understood.

The present report deals with the stoichiometry of the reaction of Ru(II) ammines with Cr^{+2}, the stoichiometry of the reaction of selected cobaltammines with $Ru(NH_3)_6^{+3}$ and $Ru(NH_3)_5^{+2}$, the oxidation–reduction potential for the $Ru(NH_3)_6^{+3}$ half-reaction, and the oxidation of $Ru(NH_3)_6^{+2}$ and $Ru(NH_3)_5^{+2}$ by ClO_4^- and various cobaltammines. A feature of particular interest to us in the work with the cobaltammines was the influence of the ionic strength on the rates of reaction of ions of different charge type.

Experiment

Complex ammines of Ru(III) were prepared and analyzed as described previously.[2] Concentrations of Ru(II) species (and of most other reducing agents) were determined by reduction of a standard solution of $Co(NH_3)_5Br(ClO_4)_2$. The concentration of $Co(NH_3)_5Br^{+2}$ was determined spectrophotometrically using for ϵ at the charge-transfer maximum (λ 252.5 mμ) the value of $1.64 \times 10^4\ M^{-1}$ cm.$^{-1}$. Measurements of pH and e.m.f. were made with a Beckman Type G pH-millivoltmeter. Ammine species of Ru(II) were prepared from the corresponding +3 ammines by Cr^{+2} or by Zn(Hg) reduction. Sodium perchlorate solutions were prepared from analytical grade Na_2CO_3 and perchloric acid. Excess acid was determined by titration with NaOH. Cupric perchlorate solutions were analyzed by EDTA titration using murexide as an indicator.[3]

All reactions were run in solutions scrubbed with deoxygenated nitrogen. Kinetics were determined spectrophotometrically. A variety of mixing techniques were used in the kinetic studies, but the most useful was the simple syringe technique described by Svatos and Taube.[4]

All reactions except where otherwise noted were carried out at 25 ± 0.2°.

Results

(A) Reduction of Ru(III) Ammines by $Cr^{+2}(aq)$.

$$Ru(NH_3)_6^{+3} + Cr^{+2} \longrightarrow Ru(NH_3)_6^{+2} + Cr^{+3} \quad (i)$$

In Table I are summarized the results of experiments done to establish the stoichiometry of the reduction of $Ru(NH_3)_6^{+3}$ by Cr^{+2}. In experiments 1–3 the product solutions were treated by cation-exchange techniques, in an effort to learn the concentrations of the Cr(III) species, their identities being established spectrophotometrically. While the cation-exchange technique as we used it was fairly satisfactory for cations of charge +2, we achieved only partial recovery of $Cr(H_2O)_6^{+3}$ from the ion-exchange column. In experiments 4–7 of Table I, the $Cr(H_2O)_6^{+3}$ concentration was estimated in the reaction mixture from the absorbance[5,6] at 474 mμ. These particular experiments were run in 5- or 10-cm. spectrophotometric cells, oxygen being excluded.

(1) F. M. Lever and A. R. Powell, Special Publication No. 12, The Chemical Society, London, 1959, p. 135.
(2) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **84**, 4984 (1962).
(3) G. Schwarzenbach, "Complexometric Titrations," Methuen and Co., Ltd., London, 1957.
(4) G. Svatos and H. Taube, *J. Am. Chem. Soc.*, **83**, 4172 (1961).
(5) J. A. Laswick and R. A. Plane, *ibid.*, **81**, 3564 (1959).
(6) H. S. Gates and E. L. King, *ibid.*, **80**, 5011 (1958).

TABLE I

STOICHIOMETRY OF THE $Ru(NH_3)_6^{+3}$–Cr^{+2} REACTION
(25°, $[H^+] \sim 10^{-2}$–10^{-3} M)

Expt. no.	$[Ru(NH_3)_6^{+3}] \times 10^3$ M	$[Cr^{+2}] \times 10^3$ M	Medium	Product species	Concn. $\times 10^3$ M	Note
1	6.19	5.57	0.19 M NaCl	$CrCl^{+2}$	5.3	*a*
2	5.02	2.83	0.020 M $NaClO_4$	$Cr(H_2O)_6^{+3}$	1.6	*a*
3	5.36	7.39	0.020 M $NaClO_4$	$Cr(H_2O)_6^{+3}$	5.0	*b*
4	0.817	0.225	...	$Cr(H_2O)_6^{+3}$	0.22 ± 0.02	*c*
5	0.794	0.390	...	$Cr(H_2O)_6^{+3}$	0.36 ± 0.02	*c*
6	0.482	0.326	...	$Cr(H_2O)_6^{+3}$	0.34 ± 0.02	*c*
7	0.158	0.415	...	$Cr(H_2O)_6^{+3}$	0.11 ± 0.02	*c*
8	0.490	0.223	...	$Cr(H_2O)_6^{+3}$	0.21 ± 0.02	*c*

[a] $HClO_4$ used in gradient elution (0.1 to 5 M). [b] NaCl used in gradient elution (0.1 to 3 M). [c] $Cr(H_2O)_6^{+3}$ absorbance measured within 5 min. of mixing, no electrolyte other than that in reagent solution.

$$Ru(NH_3)_5Cl^{+2} + Cr^{+2} \longrightarrow Ru(NH_3)_6^{+2} + CrCl^{+2} \quad \text{(ii)}$$

Experiments were also done on the stoichiometry of the reduction of $Ru(NH_3)_5Cl^{+2}$ by Cr^{+2} with $Ru(NH_3)_5Cl^{+2}$ initially at 2.83×10^{-3} M and Cr^{+2} at 1.32×10^{-3} M in perchlorate medium containing H^+ (*ca.* 10^{-3} M) and Zn^{+2} (*ca.* 0.7×10^{-3} M); the product solution was estimated by spectrophotometric means to contain 0.34×10^{-3} M $Cr(H_2O)_6^{+3}$ and 1.34×10^{-3} M $CrCl^{+2}$. By using ion-exchange methods $[CrCl^{+2}]$ in this solution was found to be 1.17×10^{-3} M. The latter value sets a lower limit on the concentration of $CrCl^{+2}$ produced, because elution from the resin is not quite complete. Both results agreed in showing that $CrCl^{+2}$ is the major product of the reaction, and despite the spectrophotometric result (which does not give an accurate differentiation of $Cr(H_2O)_6^{+3}$ and $CrCl^{+2}$) $CrCl^{+2}$ seems to represent more than 85% of the product. This conclusion is confirmed by a second experiment with $[Ru(NH_3)_5Cl^{+2}] = 0.98 \times 10^{-3}$ M, $[Cr^{+2}] = 0.75 \times 10^{-3}$ M in which spectrophotometric analysis showed that the final $[CrCl^{+2}] = 0.76 \times 10^{-3}$ M and $[Cr(H_2O)_6^{+3}] \leq 0.03 \times 10^{-3}$ M.

(B) Stoichiometry of the Oxidation of Ru(II) Ammines by Co(III) Ammines.—The Ru(II) used in the experiments outlined in this section was prepared by the reaction of Cr^{+2} in slight excess with Ru(III) ammines. When the reducing mixture was added to the Co(III) solution, there was an initial rapid reduction of Co(III), which in every case was complete within 10 sec., followed by a slower reaction, the rate of which could easily be followed. It is readily demonstrated that the first phase corresponds to the reaction of excess Cr^{+2} with Co(III), while the second phase corresponds to the reaction of Ru(II) with Co(III). The change in Co(III) concentration occurring in the second stage of reaction was obtained as the difference between $[Co(III)]_{final}$ and $[Co(III)]_0$ estimated by extrapolating [Co(III)] as a function of time in the second phase to time zero. The amount of Co(III) reduced in the initial fast reaction is not always consistent with the excess Cr^{+2} as recorded in Table II, because these experiments were not carefully enough done to eliminate in every case partial air oxidation of Cr^{+2} in these very dilute solutions.

The data of Table II show that even with excess Cr^{+2}, under our conditions, no reduced material is produced

TABLE II

STOICHIOMETRY OF Co(III)–Ru(II) REACTIONS IN EXCESS Cr^{+2}

Co(III) species	[Co-(III)][a] $\times 10^5$ M (initial)	$[Ru(NH_3)_6^{+2}]_0 \times 10^5$ M	Δ[Co(III)] $\times 10^5$ M (second phase)	Note
$Co(NH_3)_5Br^{+2}$	1.74	1.05	1.09	*b*
$Co(NH_3)_5Br^{+2}$	1.47	0.70	0.53	*b, c*
trans-$Co(en)_2Cl_2^+$	0.54	0.42	0.48	*d*
trans-$Co(en)_2Cl_2^+$	0.57	0.34	0.35	*d*

[a] Co(III) before reductions. [b] $[Cr^{+2}]/[Ru(NH_3)_6^{+3}] = 2.4$ in stock $Ru(NH_3)_6^{+2}$ solution. [c] Co(III) entirely consumed. [d] $[Cr^{+2}]/[Ru(NH_3)_6^{+3}] = 1.48$ in the stock $Ru(NH_3)_6^{+2}$ solution.

which does not react with Co(III), and, specifically, that elementary Ru is not formed during the time (up to 30 min.) that Cr^{+2} and Ru(II) are in contact.

$$5H^+ + X + Ru(NH_3)_5^{+2} + Co(NH_3)_5I^{+2} \longrightarrow Ru^{III}(NH_3)_5X + Co^{+2} + 5NH_4^+ + I^-$$

In Table III are shown the results of three experiments on the stoichiometry of the reaction of $Ru(NH_3)_5^{+2}$ [7] with $Co(NH_3)_5I^{+2}$. In this system, as in the systems reported in Table II, the stoichiometry is 1:1 within the limits of our experimental error, which in these dilute and sensitive solutions is understandably rather high.

TABLE III

THE REDUCTION OF $Co(NH_3)_5I^{+2}$ BY $Ru(NH_3)_5^{+2}$ AT 25 ± 1°[a]

$[Co(NH_3)_5I^{+2}]_0 \times 10^4$ M	$[Ru(NH_3)_5^{+2}]_0 \times 10^4$ M	$\Delta[Co(NH_3)_5I^{+2}] \times 10^4$ M
8.5	5.1[b]	5.5
8.5	5.1[b]	5.3
11.7	9.6[c]	≥ 8.7

[a] The supporting electrolyte in these three experiments was $\Sigma[SO_4^{-2}] = 0.43$ M and $[H^+] = 5 \times 10^{-3}$ M, 0.026 M HCl, and 0.029 M $HClO_4$, respectively. [b] Prepared by Zn(Hg) reduction of $[Ru(NH_3)_5Cl]SO_4 \cdot nH_2O$. [c] By reduction, as above, of $[Ru(NH_3)_5H_2O]SO_4HSO_4 \cdot nH_2O$.

The reaction of $Co(NH_3)_5I^{+2}$ with $Ru(NH_3)_5^{+2}$ was investigated further to learn whether significant amounts of $Ru(NH_3)_5I^{+2}$ are formed as the product. For these experiments, $[Co(NH_3)_5I](ClO_4)_2$ was used, and $Ru(NH_3)_5^{+2}$ was prepared by Zn(Hg) reduction

(7) Cyclic oxidation–reduction experiments described in detail in a later section demonstrate that $Ru(NH_3)_6^{+3}$ and $Ru^{III}(NH_3)_5L$ retain their respective complements of NH_3 on reduction, but the group L is in the usual case lost on reduction. Accordingly the reduced species will be represented as $Ru(NH_3)_6^{+2}$ and $Ru(NH_3)_5^{+2}$, where for the pentaammine it is understood that H_2O probably completes the coordination sphere.

TABLE IV

RECOVERY OF Ru(III) AMMINES FROM Ru(II) AMMINES WITH ClO_4^- AS OXIDANT

Initial Ru(III) species	Type of redn.	Reductant concn. $\times 10^4$ M	$[Ru(III)]_0$ $\times 10^4$ M	$[Cl^-]$, M	$[ClO_4^-]$, M	—Species identified on oxidation (at 25°)— $[Ru(NH_3)_5Cl^{+2}]$[b] $\times 10^4$ M	$[Ru(NH_3)_5OH_2^{+3}]$[c] $\times 10^4$ M	$[Ru(NH_3)_6^{+3}]$[d] $\times 10^4$ M
$Ru(NH_3)_5Cl^{+2}$	$[Cr^{+2}]$[a]	1.25	0.55	2×10^{-4}	0.060	<0.01	0.54	...
$Ru(NH_3)_5Cl^{+2}$	$[Cr^{+2}]$[a]	2.24	1.14	0.0152	0.01	0.78	0.23	...
$Ru(NH_3)_5Cl^{+2}$	$[Cr^{+2}]$[a]	2.50	1.01	0.0031	0.110	0.71	0.35	...
$Ru(NH_3)_6^{+3}$	Zn(Hg)	...	6.3	...	0.48	...	...	...

[a] The Cr^{+2} reductions of $Ru(NH_3)_5Cl^{+2}$ were carried out in the reaction mixture. Since Cr^{+2} is present in excess, and since the reaction of $Ru(NH_3)_5Cl^{+2}$ with Cr^{+2} is much more rapid than the reaction of $Ru(NH_3)_5^{+2}$ with ClO_4^{-2}, an induction period, t_I, lapsed in these experiments before Ru(III) species were observed to reappear (through oxidation by ClO_4^-). These times, t_I, are consistent with the rates of the two reactions involved and with the excess of Cr^{+2}; however, t_I values are difficult to correlate quantitatively because of uncertainties in the extinction coefficients of Ru(II) species at 327.5 mμ and because of uncertainty of the rate of the reaction of Cr^{+2} and $Ru(NH_3)_5Cl^{+2}$ under the conditions of these experiments. [b] Determined spectrophotometrically at 326.5 mμ (ϵ 1.92 $\times 10^3$ M^{-1} cm.$^{-1}$).[8] Correction made for absorption due to $Ru(NH_3)_5OH_2^{+3}$ at 327.5 mμ (ϵ 290 M^{-1} cm.$^{-1}$). [c] Determined spectrophotometrically at 268 mμ (ϵ 757 M^{-1} cm.$^{-1}$).[2] Correction made for absorption of $Ru(NH_3)_5Cl^{+2}$ at 268 mμ (ϵ 160 M^{-1} cm.$^{-1}$).[8] [d] Determined spectrophotometrically at 276 mμ.[8]

of $[Ru(NH_3)_5OH_2]SO_4HSO_4 \cdot nH_2O$. At low acid (pH >3), with Co(III) and Ru(II) each at $\sim 10^{-3}$ M, little $Ru(NH_3)_5I^{+2}$ forms, and the principal form of Ru(III) is the sulfate complex, but when the reaction medium contained 0.03 M $HClO_4$, we found in one experiment with $[Co(NH_3)_5I^{+2}]_0 = 6.8 \times 10^{-4}$ and $[Ru(NH_3)_5^{+2}] = 4.7 \times 10^{-4}$ M that 2.5×10^{-5} M $Ru(NH_3)_5I^{+2}$ formed; in a second experiment with the Co(III) and Ru(II) complexes at 1.36×10^{-3} and 4.7×10^{-4} M, we found 3×10^{-5} $M > [Ru(NH_3)_5I^{+2}] > 2 \times 10^{-5}$ M. Spectrophotometric determinations of the products of these reactions were accomplished in less than 5 min. after mixing reactant solutions.

(C) Spectra of the Reduced Species.—The visible and ultraviolet absorption spectra of reduced ruthenium ammines do not seem to have well-defined peaks; rather we have always observed two "shoulders." The first shoulder is in the range 380–420 mμ. The molar absorbancies are about 30 and 700 M^{-1} cm.$^{-1}$, respectively. These observations apply to both $Ru(NH_3)_6^{+2}$ and $Ru(NH_3)_5^{+2}$. The position of the more intense band depends somewhat on the anion present in the case of $Ru(NH_3)_5^{+2}$ and has been found to be 30–40 mμ wide in about 0.1 M Na_2SO_4. These features seem to be independent of the manner in which the Ru(III) ammine is reduced. However, since the decomposition of $Ru(NH_3)_6^{+2}$ gives a species which has a very intense absorbance (ϵ probably greater than 10^4 M^{-1} cm.$^{-1}$ at 262 mμ), we cannot be certain that $Ru(NH_3)_6^{+2}$ does not have a well-defined peak at about 280 mμ and the same reservation obtains with respect to the absorption spectra of the various $Ru(NH_3)_5^{+2}$ species. The molar extinction coefficient of $Ru(NH_3)_6^{+2}$ measured at 275 mμ has been found to be 690 (±15%) in each determination, independent of the reducing agent (Cr^{+2}, V^{+2}, and Zn(Hg) were used).

(D) Demonstration that Coordinated Ammines are Retained during Oxidation and Reduction of Ruthenium Species.—The ultraviolet–visible spectra of the various Ru(III) ammine species relevant to this study have previously been described.[2,8] The spectra of $Ru(NH_3)_5Cl^{+2}$, $Ru(NH_3)_5OH_2^{+3}$, and $Ru(NH_3)_6^{+3}$ are sufficiently distinct and intense so that these species can be determined spectrophotometrically. When $Ru(NH_3)_5^{+2}$ is oxidized, the various pentaammine Ru(III) species usually appear in their equilibrium distribution. In Table IV is summarized some of the evidence which indicates that the coordinated NH_3 groups are not lost in the oxidation–reduction reaction, nor in the time, usually 1 hr. or less, that the Ru remained in the +2 oxidation state.

Oxidations with Co(III) complexes gave results in general agreement with those summarized in Table IV, but with these oxidizing agents there were interfering absorptions in the near-ultraviolet so that the results are not very accurate.

(E) The Standard Potential for $Ru(NH_3)_6^{+2} = Ru(NH_3)_6^{+3} + e^-$.—Direct cell measurements were made against a calomel half-cell using a silver electrode immersed in the solution containing the mixture of Ru(II) and Ru(III). The ratio Ru(III)/Ru(II) was adjusted by reducing Ru(III) with Cr^{+2}, several different values of the ratio being used. The solutions were 0.036 M in $NaClO_4$ (pH 2.8) and 10^{-3} to 10^{-4} M in Ru ions. The measurements were done at 0° to slow up the reduction of ClO_4^- by Ru(II). Measurements on the Fe^{+2}–Fe^{+3} half-reaction were done under precisely the same conditions. The values of e.m.f. measured for the couples Fe^{+2}–Fe^{+3},[9] $Ru(NH_3)_6^{+2}$–$Ru(NH_3)_6^{+3}$, $Ru(NH_3)_5OH_2^{+2}$–$Ru(NH_3)_5OH_2^{+3}$ were −0.46 ± 0.01, 0.07 ± 0.01, and 0.11 ± 0.01 v., respectively, each at unit ratio of oxidized and reduced forms. If liquid junction effects are assumed to be the same in the iron as in the ruthenium cell measurements, then $Ru(NH_3)_6^{+2}$–$Ru(NH_3)_6^{+3}$ and $Ru(NH_3)_5^{+2}$–$Ru(NH_3)_5OH_2^{+3}$ are less oxidizing at 0° than Fe^{+2}–Fe^{+3} by 0.53 and 0.57 v., respectively. If, in addition, the variation of e.m.f. with temperature and ionic strength is taken

(8) H. Hartmann and C. Buschbeck, *Z. physik. Chem.*, **11**, 120 (1957). Our measurements of the positions of the maxima in the visible region agree with those of Hartmann and Buschbeck, but we find that absorption by $Ru(NH_3)_5I^{+2}$ at 538 mμ is much more intense than these authors report. We estimate ϵ for the species at 538 mμ to be 2.0×10^3 M^{-1} cm.$^{-1}$.

(9) Corrections were made only for the first hydrolysis of Fe(III). The first hydrolysis constant of Fe(III) was obtained by extrapolation of the data of Milburn[10] at μ = 0.042 to 0°. The value thus obtained is K_h = 6.5×10^{-2}. With no correction for hydrolysis the measured e.m.f. of the Fe^{+2}–Fe^{+3} couple was −0.39 ± 0.01 v.

(10) R. M. Milburn, *J. Am. Chem. Soc.*, **79**, 537 (1957).

to be the same for these three cells, then at 25° $E°$ for $Ru(NH_3)_6^{+2} = Ru(NH_3)_6^{+3} + e^-$ is -0.24 v. and for $Ru(NH_3)_5^{+2} = Ru(NH_3)_5OH_2^{+3} + e^-$ $E°$ is -0.20 v.

Equilibrium in the reaction

$$Ru(NH_3)_6^{+2} + Cu^{+2} = Ru(NH_3)_6^{+3} + Cu^+ \qquad (I)$$

can be measured directly, and we have obtained a value of E'' for $Ru(NH_3)_6^{+2}$–$Ru(NH_3)_6^{+3}$ based on such measurements. To effect the equilibration, a solution containing $Ru(NH_3)_6^{+3}$, Cu^{+2}, and Na^+ as perchlorates at known concentrations was placed over clean copper shavings at 25°. The total reducing titer was measured at intervals of 0.5–2 hr. until a limiting value was reached. The determination was made by adding an aliquot of the solution to one containing $Co(NH_3)_5Br^{+2}$ and measuring the residual oxidizing agent spectrophotometrically. Equilibrium was reached quite slowly, particularly at low ionic strength.

The summary of our results is presented in Table V.

TABLE V

THE EQUILIBRIUM $Cu^{+2} + Cu = 2Cu^+$ AT 25°

$[Cu^{+2}]$ $\times 10^3$ M	$[Cu^+]^a$ $\times 10^5$ M	$[NaClO_4]$ $\times 10^3$ M	μ $\times 10^3$	K' $\times 10^6$ M
3.0	5.2	0	6.0	0.9
9.8	8.6	0	19.6	0.75
4.2	6.2	3.42	11.8	0.92
0.135	1.15	3.42	3.69	0.98

[a] Determined from the reducing titer of Cu^{+2} solutions equilibrated over clean copper shavings.

In calculating the equilibrium quotient for reaction I we have used values of the equilibrium constant $K' = [Cu^+]^2/[Cu^{+2}]$ as determined by us at various ionic strengths (Table V). For K' at infinite dilution we find $(1.15 \pm 0.15) \times 10^{-6}$ M, which agrees closely with that reported by Fenwick[11] $(1.0 \pm 0.1) \times 10^{-6}$ M.

The values of log K, when plotted against the square root of ionic strength, yield by extrapolation $K = 0.12$ at infinite dilution. Making use of $E°$ for $Cu = Cu^{+2} + 2e^-$ and of K' at infinite dilution, $E°$ for $Ru(NH_3)_6^{+2} = Ru(NH_3)_6^{+3} + e^-$ is calculated as -0.214 v. The agreement with $E°$ estimated from the cell measurements is reasonable in view of the assumptions made in treating the cell data.

TABLE VI

THE EQUILIBRIUM QUOTIENT FOR THE REACTION $Ru(NH_3)_6^{+2} + Cu^{+2} = Ru(NH_3)_6^{+3} + Cu^+$ AT 25°

$[Ru]_t$ $\times 10^4$ M	$[Cu^{+2}]$ $\times 10^4$ M	$\frac{[Ru(II)] + [Cu(I)]}{\times 10^4\ M}$	$[NaClO_4]$ $\times 10^3$ M	K
0.78	1.01	0.512	6.14	0.09
3.11	12.5	0.90	8.24	0.11
4.06	12.0	1.05	9.85	0.13
0.348	0.84	0.205	18.8	0.19
0.304	0.49	0.102	202.	0.39

(F) The Kinetic Stability of Reduced Ru Ammines.—Solutions of Ru(II) ammines cannot be stored for long periods of time, and they lose nearly all of their reducing titer within 24 hr. The half-life for this deterioration process seems to be longer the lower the concentration of Ru(II), but is not materially altered by having a reducing agent such as Zn(Hg) or Cr^{+2}(aq) present. In relatively concentrated solutions, ~0.01 M, the solution which is originally a very pale yellow gradually becomes brilliant yellow and a black precipitate forms. The species in solution has not been identified but it is characterized by a very sharp and intense absorption maximum at 262 mμ. This species is not readily oxidized by air nor is it reduced by zinc amalgam.

We have made some qualitative observations on the decomposition of $Ru(NH_3)_6^{+2}$, and conclusions based on this work follow. Three kinds of products have been observed: (1) A brilliant blue substance (λ_{max} 590 mμ; $\epsilon_{max} > 10^3$ M^{-1} cm.$^{-1}$). (2) A substance with no absorption in the visible region of the spectrum but with a very intense maximum at 262 mμ. (3) a pentaammine Ru(III) species. At high acid, >0.5 M, products (1) and (2) predominate, and at 1 M H^+ they appear to account for about equal amounts of the Ru(II) which disappears. Products (2) and (3) prevail at low acidity, and when an oxidizing agent is present, even if like ClO_4^- or $Co(NH_3)_6^{+3}$ it reacts only very slowly with Ru(II), products of the type of (3) predominate. The half-life for the disappearance of $Ru(NH_3)_6^{+2}$ at $[H^+] \sim 10^{-6}$ M is *ca.* 50 hr. and at $[H^+] = 0.2$ M it is *ca.* 5 hr. when $[Ru(NH_3)_6^{+2}]$ is 4×10^{-4} M. The blue substance, which in fact appears to be a mixture of two species with slightly different absorption maxima, is generated quite rapidly in strong acid ($t_{1/2}$ in 4 M $H^+ \simeq 10$ min.). These blue materials persist in air but are oxidized by Co(III) ammines (rapidly even by $Co(NH_3)_6^{+3}$!) and by Cl_2.

(G) Kinetic Studies with Ruthenium(II) Species. Salt Effects.—The rates of reduction by $Ru(NH_3)_6^{+2}$ of the chloro-, bromo-, and iodopentaammines of cobalt(III) have been observed to obey the rate law

$$R = k[Ru(II)][Co(III)]$$

Integrated forms of this law have been used to determine specific rates of these reactions and in most instances fit the data to 90–95% of reaction. Reactions have been studied both in excess Co(III) and in excess $Ru(NH_3)_6^{+2}$. The following two reactions have been studied in greatest detail at a variety of ionic strengths.

$$5H^+ + Ru(NH_3)_6^{+2} + Co(NH_3)_5Br^{+2} \longrightarrow Ru(NH_3)_6^{+3} + Co^{+2} + 5NH_4^+ + Br^- \qquad (II)$$

$$2H^+ + Ru(NH_3)_6^{+2} + Co(en)_2Cl_2^+ \longrightarrow Ru(NH_3)_6^{+3} + Co^{+2} + 2enH^+ + 2Cl^- \qquad (III)$$

Reactions II and III are so rapid that by our techniques it was necessary to use very low reactant concentrations (2×10^{-5}–10^{-6} M). Under these conditions we encountered difficulty with catalytic effects which were eventually traced to Cu^{+2} and to a substance, possibly Hg_2^{+2}, which was introduced when $Ru(NH_3)_6^{+3}$ solutions were reduced over Zn(Hg). The impurities are effective when present even at 10^{-7} M or less. These catalytic effects become smaller with

(11) F. Fenwick, *J. Am. Chem. Soc.*, **48**, 860 (1926).

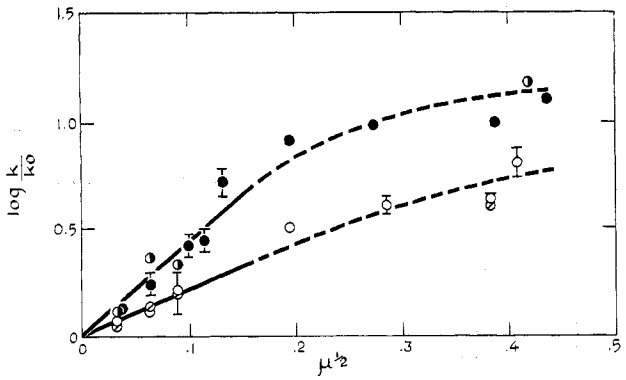

Figure 1.—Ionic strength effects in the reaction of $Ru(NH_3)_6^{+2}$ with Co(III) complexes.

Symbol	Co(III) species	k_0, M^{-1} sec.$^{-1}$
●	$Co(NH_3)_5Br^{+2}$	83
◑	$Co(NH_3)_5I^{+2}$	4.5×10^2
○	*trans*-$Co(en)_2Cl_2^+$	1.3×10^3
⊖	*cis*-$Co(en)_2Cl_2^+$	1.7×10^2

Error limits indicate the mean deviations in experiments in which two or more measurements of the specific rate were made at the indicated ionic strength. The ionic strength was adjusted with $NaClO_4$.

increasing ionic strength and do not seem to appear at all in the slower reactions which call for more concentrated solutions or in reactions performed with carefully purified materials and with $Ru(NH_3)_6^{+2}$ prepared by reduction with Cr^{+2}. All the data in Figure 1 represent experiments in which $Ru(NH_3)_6^{+2}$ was generated by reduction with Cr^{+2}. The results which are shown in Figure 1 are based on experiments done in solutions with $NaClO_4$ as the predominant electrolyte. Perchloric acid contributes significantly to ionic strength only in the most dilute solutions; $HClO_4$ and $NaClO_4$ together make up at least 75% of the ionic strength.

From data at ionic strengths less than 0.015 M we estimate for reaction II (see Figure 1)

$$\log k_1 = (4.4 \pm 0.3)\sqrt{\mu} + \log k_1^0$$

and for reaction III

$$\log k_2 = (2.5 \pm 0.3)\sqrt{\mu} + \log k_2^0$$

The slopes expected from the Brønsted–Debye–Hückel equation are 4.08 and 2.04, respectively,[12] for reactions of charge product four and two.

From a measured specific rate of 2.1×10^2 M^{-1} sec.$^{-1}$ at $\mu = 0.16$ M we estimate from Figure 1 that for the reaction of $Co(NH_3)_5Cl^{+2}$ with $Ru(NH_3)_6^{+2}$ the specific rate at infinite dilution is 17 M^{-1} sec.$^{-1}$.

(H) Reactions with ClO_4^-.—The reaction of ClO_4^- with $Ru(NH_3)_5^{+2}$ has previously been reported.[2] More complete data are shown in Table VII. The reaction was followed by spectrophotometric determination of $Ru(NH_3)_5Cl^{+2}$, the dominant form of the Ru(II) product. The specific rate k_3 in Table VII is defined by the equation

$$\frac{-d[Ru(II)]}{dt} = k_3[ClO_4^-][Ru(II)]$$

k_3 in the range covered is independent of acidity, of [Ru(II)], and, over a considerable range, of $[ClO_4^-]$. The deviation noted in expt. 130 may be ascribed in part to the increased ionic strength; that in expt. 133 to a contribution to the reaction by the spontaneous deterioration of Ru(II).

$$8H^+ + 8X + 8Ru(NH_3)_5^{+2} + ClO_4^- \longrightarrow Cl^- + 8Ru^{III}(NH_3)_5X + 4H_2O$$

The reaction of Cr^{+2} with Ru(III) is very rapid and of ClO_4^- with Ru(II) is quite rapid and thus Ru(II) or Ru(III) can be used as a catalyst for the reduction by Cr^{+2} of ClO_4^-. Reaction in a mixture containing $NaClO_4$ (1.9 M), Cr^{+2} (0.043 M), and $Ru(NH_3)_5Cl^{+2}$ (1.4×10^{-3} M) was allowed to proceed until the reducing material was exhausted. The concentration of Cl^- in the product solution was found (by weight, as AgCl) to be 8.8×10^{-3} M while that expected from the reduction of ClO_4^- by Cr^{+2} is 8.4×10^{-3} M. The agreement may to some extent be fortuitous because we are not certain whether the chloride introduced with the catalyst contributes to the total amount measured, nor whether Ru(III) is oxidized to a higher oxidation state and thus also reduces ClO_4^- in this reaction stage, but the experiment suffices to prove that ClO_4^- is indeed reduced when Ru(II) is present.

TABLE VII

THE OXIDATION OF $Ru(NH_3)_5^{+2}$ BY ClO_4^- AT 25°; [NaCl] = 0.142 M

Expt.	$[Ru]_t \times 10^5$ M	$[Cr^{+2}] \times 10^5$ M	$[NaClO_4]$, M	$[H^+]$, M	k_3, M^{-1} sec.$^{-1}$
129	8.00	3.2	3.31×10^{-3}	$<10^{-3}$	0.027 ± 0.002
130	8.41	6.15	6.61×10^{-2}	$<10^{-3}$	0.016 ± 0.006
131	8.51	2.63	1.11×10^{-2}	$<10^{-3}$	0.025 ± 0.001
132	7.85	3.76	5.52×10^{-3}	$<10^{-3}$	0.025 ± 0.001
133	8.28	4.42	6.50×10^{-4}	$<10^{-3}$	0.039 ± 0.003
134	6.21	5.11	$(3.31 \times 10^{-3})^a$	4.8×10^{-3}	0.026 ± 0.001

[a] Total perchlorate = $[NaClO_4] + [HClO_4] = 8.1 \times 10^{-3}$ M

The oxidation of $Ru(NH_3)_6^{+2}$ by ClO_4^- is slow enough so that it is complicated by spontaneous decomposition of $Ru(NH_3)_6^{+2}$. In the earlier work this complication was not appreciated, and our published estimate for the rate of the $Ru(NH_3)_6^{+2}$–ClO_4^- reaction is in error. In our present work, to maintain the rate of the side-reaction constant, a sulfate–bisulfate reaction medium ($\Sigma[SO_4^{-2}] = 0.14$) at pH 2.8 was used, and for the series of experiments, $[ClO_4^-] + [Cl^-] = 0.30$ M, except for one at 0.48 M ClO_4^-. In Figure 2, the first-order specific rates for the disappearance of $Ru(NH_3)_6^{+2}$ in solutions of varying ClO_4^- content are shown plotted against $[ClO_4^-]$. The data show that in our medium, there is a path for the spontaneous disappearance of $Ru(NH_3)_6^{+2}$ corresponding to the intercept at $[ClO_4^-] = 0$, and that a path apparently first order in $[ClO_4^-]$ also contributes to the reaction. The specific rate for the reaction ClO_4^- with $Ru(NH_3)_6^{+2}$ as defined by the rate law

$$\frac{-d[Ru(II)]}{dt} = k_4[Ru(II)][ClO_4^-] \qquad (25°\ \mu = 0.62)$$

(12) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 525.

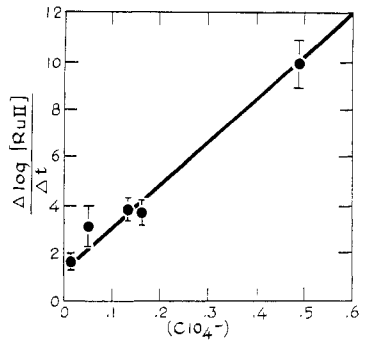

Figure 2.—The reaction of $Ru(NH_3)_6^{+2}$ with ClO_4^-. Conditions: 25.0 ± 0.2°; $[SO_4^{-2}]$ = 0.14 *M*; $[ClO_4^-]$ + $[Cl^-]$ = 0.3 *M* except in the experiment at highest $[ClO_4^-]$ (in this experiment $[ClO_4^-]$ = 0.48 *M* and $[Cl^-]$ = 0).

under our conditions is 3.0×10^{-4} M^{-1} sec.$^{-1}$. When perchlorate ion is present, we apparently have a means of studying the spontaneous decomposition of Ru(II) because the deeply colored substances which ordinarily form do not appear, and instead $Ru(NH_3)_5Cl^{+2}$ is a major product of the reaction. The intercept at $[ClO_4^-]$ = 0 corresponds to a half-life for $Ru(NH_3)_6^{+2}$ of 500 min.

(I) Variation with Acidity of the Rate of Reduction of $Co(NH_3)_6^{+3}$ by $Ru(NH_3)_5^{+2}$.—The reaction medium for this study contained 0.2 *M* NaCl. Below a pH of 5, the product was largely $Ru(NH_3)_5Cl^{+2}$ but above a pH of 6, it became $Ru(NH_3)_5OH^{+2}$. The results of the kinetic experiments are shown in Figure 3.

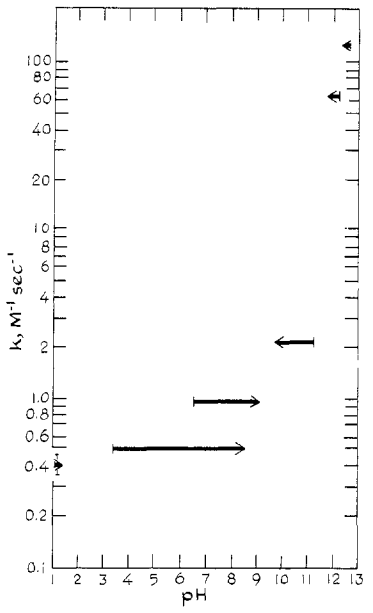

Figure 3.—Variation with pH of the specific rate of the reaction of $Ru(NH_3)_6^{+2}$ with $Co(NH_3)_6^{+3}$: medium, 0.2 *M* NaCl; |— indicates estimate of initial pH; →| indicates the measured, final pH.

Reasonable titration curves were obtained when solutions of $Ru(NH_3)_5^{+2}$ were titrated with NaOH, and they suggest as p*K* for the reaction

$$Ru(NH_3)_5OH_2^{+2} = Ru(NH_3)_5OH^+ + H^+$$

at 25° and μ = 0.2 the value 10.7.

(J) The Reduction of $Ru(NH_3)_6^{+3}$ by Cr^{+2}(aq).—The reaction of Cr^{+2} with $Ru(NH_3)_6^{+3}$ was followed by observing the change with time of the absorbance of the reaction mixture at 275 mμ. The data obtained in perchlorate media are shown in Table VIII.

TABLE VIII

THE RATE OF THE Cr^{+2}(aq)–$Ru(NH_3)_6^{+3}$ REACTION AT 25°

$[Ru(NH_3)_6^{+2}]$ × 10^4 *M*	$[Cr^{+2}]$ × 10^4 *M*	$[NaClO_4]$ × 10^3 *M*	$[HClO_4]$ × 10^3 *M*	μ, *M*	*k*, M^{-1} sec.$^{-1}$[a]
2.8	2.5	3.0	2.0	0.0074	13 ± 3
2.0	2.4	5.0	3.0	0.010	4 ± 1
1.04	4.1	11.1	7.8	0.019	12 ± 2
13.3	9.3	10.	10.0	0.031	45 ± 10
7.8	2.6	68.	6.0	0.079	99 ± 10

[a] Error estimates based on the scatter of data in the kinetic determinations.

The rate of the reaction is very sensitive to chloride ion concentration, and the rate law with chloride ion present becomes

$$\frac{d[Ru(II)]}{dt} = [k_5 + k_6[Cl^-]][Ru(NH_3)_6^{+3}][Cr^{+2}]$$

At μ = 0.055, k_5 = (84 ± 9) M^{-1} sec.$^{-1}$, k_6 = (1.2 ± 0.3) × 10^3 M^{-2} sec.$^{-1}$, and at μ = 0.022 *M*, k_5 = (28 ± 3) M^{-1} sec.$^{-1}$, k_6 = (6 ± 2) × 10^2 M^{-2} sec.$^{-1}$.

(K) Catalyzed Equilibration of Pentaammine Ru(III) Complexes.—The rapid equilibration of $Ru(NH_3)_5OH_2^{+3}$ with Cl^- to form $Ru(NH_3)_5Cl^{+2}$ was reported in an earlier communication. It should be noted that the equilibrium constant reported there [(43 ± 3) M^{-1}] is in error, and the revised value is (70 ± 6) M^{-1} (at 25°, μ = 0.11 *M*). This revised value is in fair agreement with a recent[13] estimate of *K* = 140 ± 40 M^{-1} in a *p*-toluenesulfonic acid medium (μ = 0.1). Measurements have now also been made for the iodo and bromo complexes and our recent data are summarized in Tables IX and X.

Discussion

The experiments on stoichiometry that we have done prove that the one-electron reduction of $Ru(NH_3)_6^{+3}$ or of $Ru(NH_3)_5Cl^{+2}$ is a facile process. The salt effects observed in dilute solution are consistent with a charge of +2 on the reduced species. These facts together with the proof that reoxidation forms $Ru(NH_3)_6^{+3}$ or $Ru^{III}(NH_3)_5$ support the assumption that the reduced species are $Ru(NH_3)_6^{+2}$ and $Ru(NH_3)_5^{+2}$, respectively.

It should be noted that where there is a basis for comparison our observations are in agreement with those of Lever and Powell.[1] In addition to the work done with Ru(II) solutions, we have prepared solid Ru(II) compounds by the methods outlined by them. However, the solid material does air oxidize and is more difficult to purify, manipulate, and store than the solutions which we have used in our experiments. Also, as reported in ref. 1, we find that Ru(II) prepared by any of the methods may be oxidized by Cl_2 to pentaammine and hexaammine Ru(III). However, the chlorine

(13) J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).

TABLE IX

ASSOCIATION CONSTANTS FOR $Ru(NH_3)_5OH_2^{+3} + Cl^- = Ru(NH_3)_5Cl^{+2} + H_2O$

$[Ru(III)]_0$[a] × 10^5 M	$[H^+]$ × 10^3 M	$[ClO_4^-]$, M	$[Cl^-]$, M	$[Cr^+]$ × 10^5 M	Products: $[Ru(NH_3)_5Cl^{+2}]$[b] × 10^5 M	Products: $[Ru(NH_3)_5OH_2^{+3}]$[b] × 10^5 M	K,[d] M^{-1}
10.14	0.5	0.0673	0.108	9.1	9.2	0.94[d]	91
6.55	0.5	0.0645	0.105	9.06	5.79	0.68[e]	81
8.74	0.4	0.077	0.008	6.9	3.0	5.6	67
9.25	1	0.110	0.00231	5.1	1.65	8.19	87
8.39	1	0 108	0.00114	5.5	0.788	10.0	69
8.59	1	0.107	0.00233	3.4	1.04	7.87	57
8.62	1	0.108	0.00233	4.5	1.12	7.14	67
8.63	1	0.111	0.00233	5.9	1.20	7.28	71
19.8	1	0.110	0.00250	9.5	2.94	16.7	70
16.8	1	0.106	0.00252	9.0	2.58	15.6	65

[a] Initial Ru(III) species was $Ru(NH_3)_5Cl^{+2}$ for the first four entries and $Ru(NH_3)_5OH_2^{+3}$ for the remaining five entries. [b] Concentration determined as specified in Table IV. [c] $K = [Ru(NH_3)_5Cl^{+2}]/[Ru(NH_3)_5OH_2^{+3}][Cl^-]$. [d] $[Ru(NH_3)_5OH_2^{+3}]$ too small to measure accurately and estimated as the difference between the entries in columns 1 and 4.

TABLE X

ASSOCIATION CONSTANTS FOR Br^- AND I^- AT 25°

$[Ru(III)]_0$[a] × 10^5 M	$[Cr^{+2}]_0$ × 10^5 M	$[ClO_4^-]$, M	$[Cl^-]$, M	$[Br^-]$, M	$[I^-]$, M	$[H^+]$ × 10^3 M	$[Ru(NH_3)_5Br^{+2}]$[b] × 10^5 M	$[Ru(NH_3)_5I^{+2}]$[c] × 10^5 M	K_{Br},[d,f] M^{-1}	K_I[e,f] M^{-1}
30	2.8	0.176	0.0009	0.072	...	7	19	...	25	...
7.82	2.0	...	0.0537	0.0476	...	0.1	1.6	...	26	...
27.3	1.4	0.033	...	0.0733	0.0565	1	5.0	14.6[g]	18	34
19.8	11.8	0.132	...	0.0532	0.0422	6	6.1	10.3[g]	34	72
8.52	2.9	0.0542	...	0.040	0.0207	2.2	2.2	2.5[g]	14	32
27.7	4.7	...	7.6×10^{-4}	...	0.0637	0.5	...	18[g]	...	29

[a] Initial concentration of $Ru(NH_3)_5Cl^{+2}$. In the two experiments without ClO_4^- present the entry is the net Ru(III) concentration after the reduction is complete. [b] Determined spectrophotometrically at 438 mμ (ϵ 1.92 × 10^3 M^{-1} cm.$^{-1}$). [c] Determined spectrophotometrically at 547 mμ (ϵ 2.0 × 10^3 M^{-1} cm.$^{-1}$,. [d] $K_{Br} = [Ru(NH_3)_5Br^{+2}]/[Ru(NH_3)_5OH_2^{+3}][Br^-]$. [e] $K_I = [Ru(NH_3)_5I^{2+}]/[Ru(NH_3)_5OH_2^{+3}][I^-]$. [f] $[Ru(NH_3)_5OH_2^{+3}]$ calculated as the difference between $[Ru(III)]_0$ and the sum of all concentrations of species $Ru(NH_3)_5X^{+2}$ (X = Cl^-, Br^-, I^-). $Ru(NH_3)_5Cl^{+2}$ calculated from association constant in Table IX. [g] In none of these experiments did we find spectrophotometric evidence of I_3^-. In a later experiment in which $[ClO_4^-] = 0.3$ M and in which the initial Ru species was entirely $Ru(NH_3)_5^{+2}$, there was a significant amount of I_3^- formed.

oxidation is difficult to control and there is often considerable loss of Ru to higher oxidation states.

The results of the experiments on the oxidation–reduction reactions of Ru(II)–Ru(III) feature some points of interest on which we shall now comment.

Since the coordinated ammonias remain bound when $Ru(NH_3)_6^{+2}$ is oxidized, the activated complexes for the reactions are of necessity such that normal coordination positions on the reducing agent are not preempted by the oxidizing agent. It is possible, however, that the oxidizing agent presents an electronegative group toward the face of the octahedron. Some such process seems called for at least in the reduction of ClO_4^-. It is difficult to understand the reduction of this ion by $Ru(NH_3)_6^{+2}$ as a simple electron-transfer process (even Na in liquid NH_3 does not reduce ClO_4^-). However, if it is assumed that the reducing agent accepts an oxygen atom from the oxidizing agent, the process can be understood qualitatively. In effect, O^{-2} displaces an electron pair from the $d\epsilon$ orbital of Ru(II) generating Ru(IV) with a coordination number of 7 and this then is reduced by Ru(II) to Ru(III). A spin-paired d^4 ion is well suited to accommodating seven groups geometrically arranged as specified above. When $Ru(NH_3)_5OH_2^{+2}$ is oxidized, a normal coordination position is available and possibly is used, but again it seems likely that a $2e^-$ change is generated in Ru(II) when ClO_4^- reacts.

We have been concerned with the question: Does atom or group transfer accompany the reaction of $Ru(NH_3)_5^{+2}$ with Co(III) complexes? In most systems it is difficult to get an answer because Ru(II) catalyzes the substitution reactions of Ru(III), and thus a definitive result can be expected only when the reaction of Ru(II) with Co(III) is very rapid. Our attempts with $Co(NH_3)_5C_2O_4H^{+2}$ and $Co(NH_3)_5Br^{+2}$ failed of their purpose, but with $Co(NH_3)_5I^{+2}$ we seem to have evidence for atom transfer. From the equilibrium quotient which we have measured, we estimate (using for the association constant the maximum value from Table IX) an upper limit to the concentration of iodopentaammineruthenium(III) which could be formed at equilibrium in the first of the experiments we have described as 1.6×10^{-5} M. The concentration observed, 2.5×10^{-5} M, is considerably in excess of this, and thus we conclude that at least a part of the reaction proceeds by direct group transfer. At low acid, when $[SO_4^{-2}]$ was high, little transfer was observed, perhaps because there is more rapid re-equilibration of the complexes, but also possibly because the mechanism is altered.

It would be difficult to predict just what the mechanisms of the reaction will be in any individual case when Ru(II) reacts with Co(III). Because of its electronic structure ($d\epsilon^6$) Ru(II) would appear to derive no great advantage from the bridged activated

complex using a normal coordination position, whereas Co(III) accepts a $d\gamma$ electron and therefore derives obvious benefit from the Co^{III}–X^- bond stretching that group transfer to the reducing agent requires. It is likely that group transfer and nontransfer mechanisms compete in the $Ru(NH_3)_5^{+2}$–Co(III) reactions. Even when group transfer to $Ru(NH_3)_5^{+2}$ takes place, as is indicated for the reaction with $Co(NH_3)_5I^{+2}$, the possibility exists that in the activated complex the oxidizing agent does not first substitute at a normal coordination position but that it rather attacks a face of the octahedron, so that Ru has a coordination number of 7 in the activated complex. In this context it is interesting to note that a considerable rate increase for $Ru(NH_3)_5^{+2}$ as compared to $Ru(NH_3)_6^{+2}$ is noted for $Co(NH_3)_6^{+3}$ as an oxidizing agent as it is for ClO_4^-, yet $Co(NH_3)_6^{+3}$ is so constituted that it cannot derive advantage from a normal coordination position.

Data on the rates of reduction of Co(III) complexes are germane to the issues which have been raised. The rates of reduction of Ru(III) complexes by Cr^{+2} are much less sensitive to changes in the first coordination sphere than is the case with Co(III). Thus for Co(III), comparing the chloropentaammine to the hexaammine as oxidizing agent[14,15] in reaction with Cr^{+2}, $k_{pent}/k_{hex} > 10^{10}$, while for Ru(III) the ratio is *ca.* 80.[2] The difference is presumably related to the fact that a γ electron is added in the first case but an ϵ electron in the second. The ϵ electrons avoid the ligands, while the γ electrons tend to oppose them, and thus the ligands may play a much more vital role in electron transfer when γ electrons rather than those of ϵ symmetry are added. The results reported here show that the reaction of $Ru(NH_3)_5Cl^{+2}$ with Cr^{+2} takes place with atom transfer from the oxidizing agent to the reducing agent. Monochlorochromium(III) is a major product and is formed far above its equilibrium concentration for the systems. It must be admitted, however, that this does not prove atom transfer unambiguously, because chloride ion may build up in the solution in the early stages of reaction and add to Cr^{+2} as it continues to react with Ru(III).

The reaction of $Ru(NH_3)_6^{+2}$ with Cr^{+2} is catalyzed by Cl^-, just as is the reaction of $Co(NH_3)_6^{+2}$ with the same reducing agent. The ratio of the specific rate by the chloride-dependent path compared to the chloride-independent path for $Ru(NH_3)_6^{+3}$ is *ca.* 14 (μ = 0.06), while for $Co(NH_3)_6^{+3}$ it is 150 (μ = 0.4). Because the values of ionic strength are so dissimilar for the two cases, an exact comparison for them cannot be made, but it is likely that when a correction for the ionic strength is applied, the value for $Co(NH_3)_6^{+3}$ will still be somewhat larger than that for $Ru(NH_3)_6^{+3}$. The contrast in the two rates, even when the mechanisms are similar, is expected to be somewhat greater for $Co(NH_3)_6^{+3}$ than for $Ru(NH_3)_6^{+3}$, because the reactions are slower for the former oxidizing agent. The results are consistent with the view that Cl^- affects largely the reactivity of the reducing agent. In the case of $Co(NH_3)_6^{+3}$ it is known that $CrCl^{+2}$ is formed when Cl^- is involved in the activated complex, and though proof has not been advanced for $Ru(NH_3)_6^{+3}$ it is likely that chloride ion is here involved in a similar fashion.

Just how Cl^- brings about the rate increase is not clear. It has been suggested[16] that the effect may arise because the $d\gamma$ electron of Cr^{+2} transfers more completely to Cl^- than it does to H_2O and thus its effect is different in an outer-sphere than in a bridged activated complex when it is itself not the bridging group. Manning and Jarnagin[17] have shown that the relative

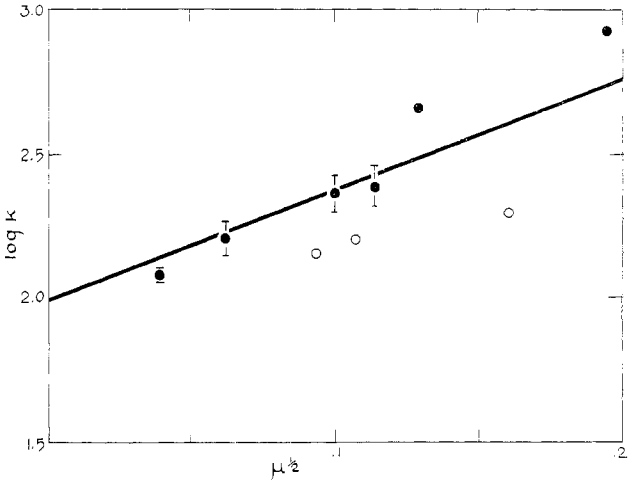

Figure 4.—Test of the Brønsted–Debye–Hückel equation for the reaction of $Co(NH_3)_5Br^{+2}$ with $Ru(NH_3)_6^{+2}$ or with Hg^{+2}: ●, $Ru(NH_3)_6^{+2}$ as reactant, present work; O, Hg^{+2} as reactant, data of Olsen and Simonsen.

effects of Cl^- and Br^- are very much the same for an outer-sphere activated complex ($Co(NH_3)_6^{+3}$ as reactant) and for a bridged activated complex ($Co(NH_3)_5O_2CCH_3^{+2}$ as the reactant) and argue on this basis that the anions play similar roles in the two reactions. They ignore, however, the fact that the outer-sphere reactions are more sensitive to the replacement of H_2O by Cl^- (or Br^-).

The variation with acidity of the rate of the $Ru(NH_3)_5^{+2}$–$Co(NH_3)_6^{+3}$ reaction does not admit of an easy explanation. The rate increases with increasing alkalinity beyond the point at which $Ru(NH_3)_5^{+2}$ is converted to $Ru(NH_3)_5OH^+$, and thus the effect is not caused simply by a greater reactivity of the latter species compared to the former. It is possible that proton dissociation from the Co(III) complex is connected with the continued rate increase as $[OH^-]$ increases, which becomes marked approaching a first-order dependence. Qualitatively, there is a striking difference in the behavior of the $Co(NH_3)_5OH_2^{+3}$–$Ru(NH_3)_6^{+2}$ reaction compared to that under present discussion, for in the former system the hydroxo complex is found to react less rapidly than the aquo. The rate of the $Ru(NH_3)_6^{+2}$–$Co(NH_3)_6^{+3}$ reaction has not

(14) J. P. Candlin, J. Halpern, and D. T. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

(15) A. Zwickel and H. Taube, *ibid.*, **83**, 793 (1961).

(16) H. Taube, Welch Foundation Conference, Modern Inorganic Chemistry, Houston, Texas, 1961.

(17) P. V. Manning and R. C. Jarnagin, *J. Phys. Chem.*, **67**, 2884 (1963).

been studied over such a large range in acidity as has that for $Ru(NH_3)_5^{+2}$ with $Co(NH_3)_6^{+3}$. In the pH range from 2 to 9, the rates of the two reactions are about equally sensitive (or insensitive) to pH, the rate increasing by only a factor of 4 or so in this pH range.

The reactions of $Ru(NH_3)_6^{+2}$ with Co(III) ammines has given us an opportunity to study kinetic salt effects in dilute solution. One of the reactions, namely that in which $Ru(NH_3)_6^{+2}$ reduces $Co(NH_3)_5Br^{+2}$, is of the same charge type as (and in fact has a reactant in common with) a system which Olson and Simonson[18] have investigated.

The data of Olson and Simonson for the reaction of Hg^{+2} with $Co(NH_3)_5Br^{+2}$ are shown together with our own in a plot of log k against $\sqrt{\mu}$ in Figure 4. Only those of Olson and Simonson's data which refer to a medium containing $NaClO_4$ as the predominant electrolyte are included. From these latter data for ionic strengths less than 0.026 M, we estimate

$$\log k_7 = (2.5 \pm 0.3)\sqrt{\mu} + \log k_7^0$$

(where the error limits on the slope reflect the nonlinearity of the dependence of log k_7 on $\mu^{1/2}$). Our own data over the total range of ionic strengths less than 0.028 M fit the analogous equation with a slope of 4.4 ± 0.3, which is somewhat more consistent with the Brønsted–Debye–Hückel equation. The Brønsted–Debye-Hückel equation thus seems applicable over a greater range of ionic strengths when $Ru(NH_3)_6^{+2}$ reacts with $Co(NH_3)_5Br^{+2}$ than when the reactant is Hg^{+2}.

Acknowledgments.—This work was supported by the National Science Foundation under Grant No. G-20954. The spectrophotometer used was purchased under Grant No. G-22611 from the National Science Foundation.

(18) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

CONTRIBUTION NO. 981 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE

Ethylene Exchange in Zeise's Anion

BY RICHARD CRAMER

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N.m.r. studies show that complexed ethylene in Zeise's anion, $[(C_2H_4)PtCl_3]^-$, exchanges at a rate >70 sec.$^{-1}$ at temperatures as low as −75°. These results were qualitatively substantiated by tracer experiments. A description is given of a $SnCl_2$-catalyzed synthesis of Zeise's salt.

Olefin displacement from complexes of platinum(II) is a rapid reaction. Thus, a number of analogs of Zeise's salt, $K[(CH_2{=}CH_2)PtCl_3]H_2O$, have been prepared by treating it with various olefins.[1] Reaction occurs readily, the volatility of ethylene tending to

$$[(CH_2{=}CH_2)PtCl_3]^- + \text{olefin} \longrightarrow [(\text{olefin})PtCl_3]^- + C_2H_4 \quad (1)$$

drive it to completion. Also, in comparing the coordinating ability of various substituted styrenes by measuring the equilibrium constant of reaction 2, Joy and Orchin noted that, at 25°, equilibrium is attained in the

$$[(\text{1-dodecene})PtCl_3]^- + XC_6H_4CH{=}CH_2 \longrightarrow [(XC_6H_4CH{=}CH_2)PtCl_3]^- + \text{1-dodecene} \quad (2)$$

few minutes required to prepare the solution for study.[2] Further, C_2D_4 was found to equilibrate with coordinated C_2H_4 in the related platinum(II) complex, $[(C_2H_4)PtCl_2]_2$, within 15 min. at temperatures as low as −15°.[3] In order to define more precisely the rate of ethylene exchange we have examined the n.m.r. spectra of solutions containing both $[(C_2H_4)PtCl_3]^-$ and free C_2H_4.

Ethylene dissolved in 1 M methanolic HCl has a proton n.m.r. absorption at δ −5.37 p.p.m. relative to tetramethylsilane (internal standard). In the same medium, coordinated ethylene in $[(C_2H_4)PtCl_3]^-$, Zeise's anion, absorbs at δ −4.83 p.p.m.[4] A solution containing both $[(C_2H_4)PtCl_3]^-$ and uncoordinated ethylene has a single n.m.r. proton absorption. The position of this absorption varies with the ratio *free* C_2H_4/*coordinated* C_2H_4 and shifts toward −5.37 p.p.m. as the ratio increases. Since the spectra were measured using an oscillator frequency of 60 Mc. sec.$^{-1}$, the exchange rate ($>(\pi\delta_{AB}H)\sqrt{2}$) is faster than 70 sec.$^{-1}$.[5] The n.m.r. spectra were recorded at temperatures down to −75° to find if the ethylene exchange rate would become so slow that absorptions due to free and coordinated ethylene would be separated. Although the n.m.r. signal broadened, it did not split but shifted

(1) J. S. Anderson, *J. Chem. Soc.*, 1042 (1936).

(2) (a) J. R. Joy and M. Orchin, *J. Am. Chem. Soc.*, **81**, 305 (1959); (b) J. R. Joy and M. Orchin, *ibid.*, **81**, 310 (1959).

(3) A. S. Gow, Jr., and H. Heinemann, *J. Phys. Chem.*, **64**, 1574 (1960).

(4) This absorption is in fact the central line of a triplet. The satellites located 17 c.p.s. above and below the central peak are caused by spin–spin splitting by Pt^{111} (spin 1/2 and natural abundance 34%). They were observed by B. D. Powell and N. Sheppard [*J. Chem. Soc.* 2519 (1960)].

(5) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 63.