the gas was analyzed by gas chromatography which revealed the formation of 20 mmol of ethane and butane.

d. Dimerization of Ethylene and Propylene. To $CoH(N_2)(PPh_3)_3$ (0.55 g, 0.63 mmol) was added 10 ml of *m*-xylene saturated with ethylene in a sealed system and the complex was dissolved with stirring. The decrease of the initial ethylene pressure (710 mm) was followed by using a mercury manometer. After the reaction proceeded for 32 hr at 26.5–29.6° the gaseous products were separated from the solution and analyzed. The formation of 40.6 mmol of butenes (*trans*-2-butene, 72%; *cis*-2-butene, 26%; 1-butene, 2%) and 0.57 mmol of ethane was observed. A similar experiment with 0.79 g (0.92 mmol) of **1** in 30 ml of *m*-xylene at 0° with an initial ethylene pressure of 700 mm (179 mmol) for 24 hr produced 26 mmol of butenes and 0.84 mmol of ethylene trimers.

Addition of 2.7 mmol of tri-*n*-butylphosphine to 0.92 mmol of **1** caused a decrease in the yield of butenes from 13 mmol in the absence of tri-*n*-butylphosphine to 9.0 mmol in the presence of the ligand.

The dimerization of propylene was carried out analogously to the dimerization of ethylene. In a typical dimerization experiment, 190 mmol of propylene with an initial pressure of 753 mm was brought in contact with 0.32 mmol of **1** in 7 ml of *m*-xylene for 47 hr at 25°, and about 17 mmol of propylene dimers was produced. The product as identified by gas chromatography contained 72.5% 2-methyl-1-pentene, 17.6% 4-methyl-*trans*-2-pentene, 2.2% 2-methyl-2-pentene, 2.1% 4-methyl-*cis*-2-pentene, and 1.1% of unidentified propylene dimers, in addition to a small amount of propane. The formation of 2-methyl-1-pentene was also confirmed by nmr and ir spectroscopy after its separation by preparative gas chromatography.

e. Isomerization of Butene. In a similar manner to the dimerization of ethylene and propylene the isomerization of 14.8 mmol of 1-butene by 1 mmol of $CoH(N_2)(PPh_3)_3$ in 30 ml of *m*-xylene was carried out at 25°. The compositions of the gas phase and the liquid phase were analyzed by taking out the samples by a hypodermic syringe after appropriate intervals.

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Kinetics and Mechanisms of the Reduction of Cobalt(III) Complexes by Uranium(III) Ions[1a]

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Abstract: Kinetics studies have been carried out on the reduction of Co(III) complexes by U^{3+} in perchloric acid solutions. The $Co(NH_3)_5X^{2+}$-type complexes react at relative rates strongly suggesting an inner-sphere mechanism, on the basis of the extent of stabilization of the transition state by different X groups. For X = H_2O the $[H^+]$ dependence suggests that an OH-bridged precursor complex is formed, the stability of which has a marked effect on the reaction kinetics. $Co(NH_3)_6^{3+}$ reacts by an outer-sphere mechanism, and its reaction is strongly catalyzed by free anions, most markedly by F^- and NCS^-. The complexes $Co(NH_3)_5NO_3^{2+}$ and $Co(NH_3)_5NO_2^{2+}$ suffer ligand reduction as well as Co(III) reduction.

Transition metal ions such as Cr^{2+}, V^{2+}, Fe^{2+}, Eu^{2+}, $Cr(bipy)_3^{2+}$, $Ru(NH_3)_6^{2+}$, $Co(CN)_5^{3-}$, and Cu^+ readily reduce Co(III) complexes. Recent years have seen extensive kinetic studies on these reactions, leading not only to the fundamental distinction between the inner-sphere and outer-sphere mechanisms, but also to the resolution, at least in part, of the factors controlling the mechanism adopted and the reaction rate.[2–4] We have sought to extend the studies to include novel and previously unstudied metal ions such as Yb^{2+} and U^{3+}, reactions of the latter being the subject of this paper. A preliminary report of part of this work has been published.[5]

Typical of the reactions whose kinetics have been studied is the reduction of $Co(NH_3)_5Br^{2+}$ according to the equation

$$Co(NH_3)_5Br^{2+} + U^{3+} + 5H^+ = Co^{2+} + U^{4+} + 5NH_4^+ + Br^- \qquad (I)$$

The chemistry of U^{3+}_{aq} has not been widely studied, possibly because textbooks refer to it being quite unstable. Although U^{3+} is a strong reducing agent

$$U^{4+} + e^- = U^{3+} \qquad E^0 = -0.63\ V^6$$

clearly capable of reducing $H_2O(H_3O^+)$ to hydrogen and perchlorate ion to chloride ion, these reactions proved to be negligible, as reported by Sato.[7] For the reactions studied here, most of which were fairly rapid, no deterioration of the U(III) solutions was noted over several hours.

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(1) (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission, Contribution No. 2792; (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

(2) Recent reviews are: (a) N. Sutin, *Annu. Rev. Phys. Chem.*, **17**, 119 (1966); (b) A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, 10, 153 (1968); (c) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968); (d) H. Taube and E. S. Gould, *ibid.*, **2**, 321 (1969).

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Definite evidence can be obtained in certain cases for inner-sphere and outer-sphere transition states.[8,9] More often the direct tests are not feasible. This is the case with U^{3+}, and indirect evidence concerning the mechanisms was therefore sought, based in part on the relative rates of different reactions.

The Co(III) complexes studied here consist of four general classes of compounds: (1) the acidopentaammine complexes, $Co(NH_3)_5X^{2+}$ (X = halide or pseudohalide), and related complexes such as $Co(en)_2Cl_2^+$, (2) the hexaammine ions, such as $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$, which necessarily react by outer-sphere mechanisms, (3) the aquoammine complexes such as $Co(NH_3)_5H_2O^{3+}$, and (4) complexes containing ligands capable of reduction by U^{3+}, *e.g.*, $Co(NH_3)_5(HC_2O_4)^{2+}$, $Co(NH_3)_5ONO_2^{2+}$.

Experimental Section

Materials. Dilute solutions of U^{3+} were prepared from U^{4+} or UO_2^{2+} (as perchlorates) usually by reduction with amalgamated zinc and occasionally by electrolytic reduction at a mercury pool cathode. The olive-green solutions of U^{3+} readily revert to U^{4+} on contact with air, and were prepared and handled under nitrogen which had been purified by Cr^{2+} scrubbing solutions. No difficulties were encountered from the inherent instability of the U^{3+} solutions to reduction of H_2O or of ClO_4^-, although no attempt was made to store them for long periods. The $UO_2(ClO_4)_2$ solutions were made by dissolving U_3O_8 in perchloric acid with heating, from which $U(ClO_4)_4$ could be prepared by electrolytic reduction. Similar results were obtained when recrystallized $UO_2(ClO_4)_2$ (G. F. Smith) was used.

The Co(III) complexes used in this study were prepared and purified according to methods given in the literature.[10-21] The compounds (R = $Co(NH_3)_5$) $[RCl]Cl_2$,[10] $[RNO_3](NO_3)_2$,[11] $[RNO_2]Cl_2$,[12] $[RONO]Cl_2$,[13] $[ROAc](OAc)_2$,[14] $[RNH_3]Cl_3$,[16] $[Co(en)_3]Cl_3$,[17] and *trans*-$[Co(en)_2Cl_2]Cl$[18] were converted to their perchlorates with sodium perchlorate or perchloric acid and recrystallized as such. Other compounds were either obtained as perchlorates by published methods, $[RHC_2O_4](ClO_4)_2$[15] and *cis*-$[Co(NH_3)_4(H_2O)_2](ClO_4)_3$,[20] or were used with other anions as in the case of *cis*-$[Co(en)_2(H_2O)Cl]SO_4 \cdot 2H_2O$[19] and *trans*-$[Co(en)_2(NH_3)(H_2O)]Br_3 \cdot H_2O$.[21] Still other complexes were prepared as cited previously:[3] $[RBr]Br_2$, $[RN_3](ClO_4)_2$, $[RNCS](ClO_4)_2$, $[RF](ClO_4)_2$, $[RH_2O](ClO_4)_3$, $[RCN](ClO_4)_2 \cdot {}^1/_2H_2O$, *trans*-$[Co(NH_3)_4(H_2O)CN]Cl_2$, and *cis*-$[Co(en)_2Cl_2]Cl$.

The identity and purity of each cobalt complex were established by analysis and by its visible–uv absorption spectrum, which agreed well with the literature values.[22]

Rate Procedures and Kinetic Data. The more rapid reactions were followed by the stopped-flow method, whereas those having half-times longer than *ca.* 5 sec were followed using a Cary Model 14 recording spectrophotometer.[3,23] Depending on the reagent in excess and the spectrum of the particular Co(III) complex being studied, the rate studies were carried out at one of the wavelengths of maximum Co(III) absorption or at an absorption maximum for U(III), λ 725 nm (ϵ 51.3 M^{-1} cm^{-1}), 522 (154), 350 (1580), and 328 (1620).[24]

Most rate experiments were carried out under pseudo-first-order conditions with the initial concentration of either U^{3+} or Co(III) in at least tenfold excess over the other. For the fastest reactions, comparable concentrations of the two (second-order conditions) were employed. All the kinetic data conformed to a second-order rate law

$$-d[U^{3+}]/dt = -d[Co(III)]/dt = k_2[U^{3+}][Co(III)] \quad (1)$$

for which the rate constants were derived according to the equations given previously.[3] A stopped-flow determination was repeated three or four times with a given set of solutions, the average deviation from the mean usually being $\leq 3\%$. The runs carried out using the Cary spectrophotometer were repeated at least twice in most instances. Thus the rate constants by both methods represent values that have been verified by appropriate checks.

The initial attempts at rate studies were interferred with by an extraneous absorbance change at λ 350 nm, found to accompany the dilution of the U^{3+} solutions at constant [H$^+$]. This process, which had a [H$^+$]-dependent decay time of the order of 0.1 sec, could be suppressed, however, by diluting a U^{3+} solution having X M H$^+$ with an equal volume of a solution containing $(\sqrt{2} - 1)X$ M H$^+$. An equilibrium giving a small concentration of a 4+ dimer

$$2U^{3+} + 2H_2O = U(OH)_2U^{4+} + 2H^+ \quad (II)$$

could account for this observation; the nature of the hydrolytic process is still under investigation. (A limit on K_{II} cannot be set because the extinction coefficient is not known.) The kinetic data on the Co(III) reactions refer to [H$^+$] dilutions made to eliminate the interference, whatever its cause.

Stoichiometry and U^{3+} Analyses. Dilute U^{3+} solutions were analyzed during kinetic runs by reaction with RBr^{2+}. Samples of U^{3+} were taken from the reactant reservoir using a small syringe (0.5–2 ml) and a 20-cm Teflon syringe needle, carefully purged with nitrogen and prerinsed with the U^{3+} solution. The samples were each delivered under the surface of RBr^{2+} solutions in dilute (0.01–0.1 M) perchloric acid, contained in small volumetric flasks which were being purged with purified nitrogen. The solutions were analyzed for [RBr^{2+}] using its peak at λ 253 nm (ϵ 1.67 × 10^4 M^{-1} cm^{-1}); the decrease in [RBr^{2+}] compared to untreated samples gives directly the U^{3+} concentration. The analyses proved reproducible to within *ca.* 3% for 10^{-4} M U^{3+} stock solutions if the RBr^{2+} concentration and the U^{3+} sample size were adjusted such that 30–70% of the RBr^{2+} originally present was reduced.

The 1:1 stoichiometry of this reaction was verified by analyzing[25] the excess of RBr^{2+} as above, assuming quantitative reduction of the uranium stock solution to U(III). The assumption was verified by the agreement of the published molar absorptivities.[24] The stoichiometry was also checked by analyzing[25] the Co(II) produced; 1.03 ± 0.03 mol of Co(II) was produced per mole of added U(III). The kinetic data also support reaction I, because the pseudo-first-order experiments lead to the same values of k_2 irrespective of whether U^{3+} or RBr^{2+} is in excess, as do the runs having comparable concentrations, where the rate constant values are based on the difference $|[RBr^{2+}]_0 - [U^{3+}]_0|$ (which assumes a 1:1 stoichiometry).

This reaction taken as a standard, other reactions were studied by analyzing the excess U^{3+} with RBr^{2+}. In the case of $RNCS^{2+}$, the amount of NCS$^-$ released in reaction with U^{3+} was also determined by passing the reaction products through a cation-exchange column. The free NCS$^-$ was then complexed by excess Fe^{3+} and its concentration determined spectrophotometrically ([Fe^{3+}] ~ 3 × 10^{-2} M, [NCS$^-$] ~ 10^{-5} M, [H$^+$] = 1 M, ϵ 3.6 × 10^3 M^{-1} cm^{-1} for $FeNCS^{2+}$ at 460 nm).[26] The stoichiometry was

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Table I. Rate Constants for $Co(NH_3)_5X^{2+}$-Type Complexes[a]

Complex	$[H^+]$,[b] M	$[Co(III)] \times 10^4$,[b] M	No. of experiments[c]	k_2,[d] M^{-1} sec^{-1}
$Co(NH_3)_5Br^{2+}$	0.012–0.194	0.20–20.2	30	$1.42 \pm 0.01 \times 10^4$
$Co(NH_3)_5Cl^{2+}$	0.015–0.190	0.18–6.61	9	$3.24 \pm 0.05 \times 10^4$
$Co(NH_3)_5N_3^{2+}$	0.010–0.190	0.25–0.85	5	$1.08 \pm 0.08 \times 10^6$
$Co(NH_3)_5F^{2+}$	0.010–0.190	0.80–1.51	6	$5.40 \pm 0.13 \times 10^5$
$Co(NH_3)_5OAc^{2+}$	0.010–0.190	4.72–12.3	6	$1.50 \pm 0.14 \times 10^4$
$Co(NH_3)_5CN^{2+}$	0.010–0.190	6.36–18.1	7	$3.45 \pm 0.22 \times 10^3$
$Co(NH_3)_5NCS^{2+}$	0.020–0.190	5.39–9.26	7	18.2 ± 0.6
cis-$Co(en)_2Cl_2^+$	0.010–0.190	2.09–5.67	5	$2.15 \pm 0.05 \times 10^4$
trans-$Co(en)_2Cl_2^+$	0.010–0.190	0.94–2.0	5	$2.15 \pm 0.08 \times 10^5$
cis-$Co(en)_2(H_2O)Cl^{2+}$	0.015–0.190	2-3–4.9	7	$1.94 \pm 0.06 \times 10^4$
trans-$Co(NH_3)_4(H_2O)CN^{2+}$	0.010–0.190	6.8	3	$\sim 8 \times 10^4$

[a] 25.0°, $\mu = 0.20$ M. [b] The range of initial concentrations in different experiments. [c] The number of independent experiments each of which represent three to four determinations. [d] The uncertainty represents the average deviation from the mean of the individual values.

thus confirmed[22] for RCl^{2+}, RN_3^{2+}, and $RNCS^{2+}$; it was then assumed to hold for the other complexes. It was also confirmed for $RHC_2O_4^{2+}$ and $RONO^{2+}$, where free oxalic and nitrous acids both react rapidly with U^{3+}. On the other hand, considerable ligand reduction occurs in the complexes $RONO_2^{2+}$ and RNO_2^{2+},[22] resulting in the consumption of >1 mol of U^{3+}/mol of Co(III).

Results

Complexes of the RX Type. The average rate constants for complexes of the pentaammine and tetraammine type are summarized in Table I, the results of the individual runs being available elsewhere.[22] The kinetic data are in accord with the second-order rate expression given by eq 1. For most of the complexes the rate constant was independent of $[H^+]$ over the range studied, typically 0.01 or 0.02–0.19 M. This not only indicates no appreciable hydrogen-ion-dependent rate term, but it establishes that for general reactions of this type the trading of H^+ and Li^+ at constant ionic strength has no appreciable rate effect (the latter point being important in considering the results on RH_2O-type complexes in a subsequent section).

The rate constant for RBr^{2+} was independent of the use of $[RBr]Br_2$ or $[RBr](ClO_4)_2$, which confirmed that the Br^- liberated during the reaction had no important effect. Addition of 0.01 F HBr to the RBr^{2+} solution increased the rate by only 15%, and 0.05 F HCl caused a 30% increase in the rate constant for the RCl^{2+} reaction. These effects of anions were not explored in detail. They suffice to show that U(III)–X complexes are probably reactive, but also that at the level of (X^-) present in the kinetic runs, X^- catalysis is negligible.

A small SO_4^{2-} catalytic path for the reduction of *cis*-$Co(en)_2(H_2O)Cl^{2+}$ was noted, the complex being used as the sulfate salt. Extrapolated to zero sulfate concentration, the rate constant is 1.8×10^4 M^{-1} sec^{-1} at 25.0°, $[H^+] = 0.05$ M. This aquo complex also appears to show a slight rate dependence on $[H^+]$, the extremes being $k_2 = 1.8 \times 10^4$ at 0.19 M H^+, and 2.1×10^4 at 0.015 M H^+. This small variation is relevant to later results on aquo complexes, as is the related trend for *trans*-$Co(NH_3)_4(H_2O)CN^{2+}$, $10^{-4}k_2$ being 9.1 ± 0.3 (0.01 M H^+), 8.7 ± 0.8 (0.05 M H^+), and 7.9 ± 0.4 (0.19 M H^+). The significance of these small $[H^+]$ effects will be considered with the results on the aquo complexes.

Complexes of the CoN_6^{3+} Type. The reactions of $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ were found to follow the same second-order rate expression as the other complexes. The experiments covered the concentration range $1.1\text{–}1.9 \times 10^{-3}$ M $Co(NH_3)_6^{3+}$ and 0.01–0.20 M H^+, the average rate constant being 1.32 ± 0.04 M^{-1} sec^{-1} for eight runs.[22] Similar experiments in $Co(en)_3^{3+}$ gave $k_2 = 0.133$ M^{-1} sec^{-1} (three experiments).

The reactions were strongly catalyzed by anions, however, as has been noted for other reactions involving this general group of Co(III) complexes.[27] A plot of the apparent second-order rate constant *vs.* $[X^-]$ for Cl^-, Br^-, and I^- is shown in Figure 1. The linear plots correspond to the relation

$$k_{app} = k_2 + k_X[X^-] \qquad (2)$$

where k_2 is the value of the second-order rate constant in perchlorate solution, and k_X is the catalytic rate constant for a particular halide ion. Values of k_X are 21.8 M^{-2} sec^{-1} (Cl^-), 6.50 (Br^-), and 4.0 (I^-). (Note that the I^- catalysis was studied in a $NaClO_4$–NaI medium, $\mu = 0.200$, and gives a slightly different value of k_2, 1.0 M^{-1} sec^{-1}.)

Consistent with this ordering of catalytic efficiency, very small concentrations of HF exert marked catalytic effects. In this case the concentration of hydrogen ion exerts an inhibiting effect. The kinetic data are consistent with the equation

$$k_{app} = k_2 + k_{HF}[HF]/[H^+] \qquad (3)$$

Figure 2 illustrates a plot of $k_{app} - k_2$ *vs.* $[HF]/[H^+]$ which is linear within the error of the data, giving $k_{HF} = 3.1 \times 10^3$ M^{-1} sec^{-1}.

The dependence on $[HF]/[H^+]$ is equivalent to a dependence on $[F^-]$, related by the acid dissociation constant. On that basis eq 3 is equivalent to eq 2; using $K_a(HF) = 1.3 \times 10^{-3}$ M,[28] $k_F = 2.4 \times 10^6$ M^{-2} sec^{-1}.

For SCN^-, the values of k_{app} are 7.92 M^{-1} sec^{-1} (at 0.0100 M SCN^-), 16.4 (0.020), 28.2 (0.030), 45.6 (0.040), and 221 (0.100). The effect of this anion can be accounted for only by adding terms in higher powers to $[SCN^-]$ to eq 2. An extensive study was not carried

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[27] A. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, **81**, 1288 (1959).

[28] Interpolated to the approximate conditions applicable here (25.0°, $\mu = 0.200$ M) from data tabulated by L. G. Sillen, *Chem. Soc., Spec. Publ.*, **No. 17**, 257 (1964).

Table II. Rates of Reduction of Aquoammine–Cobalt(III) Complexes by U^{3+} [a]

$[Co(III)]_0$, $M \times 10^4$	$[U^{3+}]_0$, $M \times 10^4$	$[H^+]$, M	k_2,[b] M^{-1} sec^{-1}	$[Co(III)]_0$, $M \times 10^4$	$[U^{3+}]_0$, $M \times 10^4$	$[H^+]$, M	k_2,[b] M^{-1} sec^{-1}
$Co(NH_3)_5H_2O^{3+}$				*cis*-$[Co(NH_3)_4(H_2O)_2{}^{3+}]$			
11.6	0.95	0.0100	43.1 ± 0.8	24.8	1.0	0.0100	303 ± 4
13.1	0.95	0.0120	41.7 ± 0.1	25.2	1.0	0.0200	284 ± 3
12.7	0.05	0.0150	38.5 ± 0.4	25.1	1.0	0.0500	257 ± 6
11.6	0.95	0.0200	36.6 ± 0.4	24.8	1.0	0.100	242 ± 7
11.3	0.95	0.0300	33.4 ± 0.1	25.3	1.0	0.180	223 ± 10
11.7	0.84	0.0500	30.8 ± 0.9	*trans*-$[Co(en)_2(NH_3)H_2O^{3+}]$			
11.9	0.95	0.0500	30.6 ± 0.2	11.4	1.07	0.0100	172 ± 7
49.4	0.46	0.0500	31.3	11.0	1.07	0.0200	127 ± 8
80.4	0.46	0.0500	33.4	11.3	1.07	0.0500	70.3 ± 1.6
12.6	0.95	0.100	28.4 ± 1.2	9.28	1.07	0.100	40.1 ± 0.1
12.0	0.95	0.150	26.2 ± 0.4	11.1	1.07	0.140	27.1 ± 0.5
12.9	0.84	0.192	26.0 ± 0.7	20.4	1.07	0.187	21.8 ± 0.7
12.2	0.95	0.196	25.5 ± 0.5	11.8	1.07	0.193	18.5 ± 0.2

[a] 25.0°, $\mu = 0.200$ M. [b] Uncertainty is the average deviation from the mean in repeat determinations.

out, however, and would require a more complete knowledge of U(III)–thiocyanate interactions.[29]

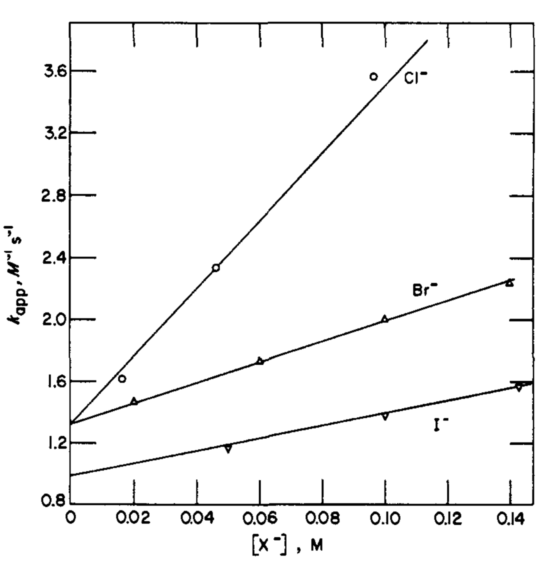

Figure 1. The catalytic effect of free halide ion on the reaction of $Co(NH_3)_6{}^{3+}$ and U^{3+} according to eq 2. The data refer to 25.0°, $\mu = 0.200$ M, with a Li^+ medium for Cl^- and Br^-, and a Na^+ medium for I^-.

Aquoammine Complexes. Complexes containing one or two coordinated water molecules are considered separately because the rates were dependent on hydrogen ion concentration. Very small effects of varying $[H^+]$ were described earlier for *cis*-$[Co(en)_2(H_2O)Cl^{2+}]$ and *trans*-$[Co(NH_3)_4(H_2O)CN]^{2+}$, both of which contain another potential bridging anion, however. The effects of varying $[H^+]$ were small, however, easily within the range where the variations might be attributed to a "medium effect," that is, to a failure of activity coefficients to remain unchanged as $[H^+]$ and $[Li^+]$ are varied at constant ionic strength.

When the only potential bridging ligand is a water molecule, however, the effects of $[H^+]$ variation are much more pronounced. Three such complexes were studied: $Co(NH_3)_5H_2O^{3+}$, *cis*-$[Co(NH_3)_4(H_2O)_2{}^{3+}]$, and *trans*-$[Co(en)_2(NH_3)H_2O^{3+}]$. Each of these compounds[30] shows a rate that increases as $[H^+]$ decreases, although the extent of the effect differs among the group. Table II summarizes the values of the apparent second-order rate constants as a function of hydrogen ion concentration.

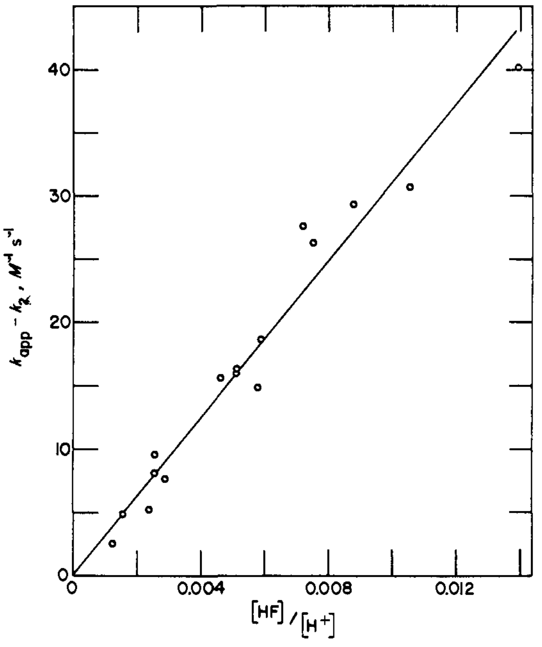

Figure 2. The effect of varying HF and H^+ concentrations on the reaction of $Co(NH_3)_6{}^{3+}$ with U^{3+} are interpreted in terms of F^- catalysis as in eq 3.

The data are consistent with a dependence on $[H^+]$ between 0 and −1 order, as shown in Figure 3. The magnitude of the effect varies, but for at least two of the complexes the deviations are outside the range where they could be accounted for by medium effects of a reasonable size. Moreover, the interpretation that this is a medium effect seems highly unlikely because the reac-

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[29] K for $U^{3+} + SCN \rightleftharpoons UNCS^{2+}$ is *ca.* 4 at $\mu = 1.0$ M: J. Templeton and J. H. Espenson, unpublished observations.

[30] J. D. White and T. W. Newton (private communication) have also studied the reaction of *cis*-$Co(NH_3)_4(H_2O)_2{}^{3+}$ with U^{3+}.

Table III. Rate Parameters for the Reduction of Aquoammine Complexes of Co(III) by U(III)[a]

Complex	A, sec^{-1}	B, M^{-1} sec^{-1}	C, M
$Co(NH_3)_5H_2O^{3+}$	0.82 ± 0.21	23.8 ± 0.9	0.015 ± 0.005
cis-$[Co(NH_3)_4(H_2O)_2{}^{3+}]$	13.4 ± 4.2	202 ± 9	0.041 ± 0.014
trans-$[Co(en)_2(NH_3)(H_2O)^{3+}]$	4.6 ± 0.1	0	0.0165 ± 0.0010

[a] At 25.0°, $\mu = 0.200$ M ($LiClO_4$).

tion rates of the very similar complexes RX^{2+} and $Co(NH_3)_6{}^{3+}$ are completely insensitive to variations in $[H^+]$ over the same concentration range in the identical medium. Equally unsuitable would be the proposal of a different rate expression for each of the three complexes, although the effect is small enough, especially for $Co(NH_3)_4(H_2O)_2{}^{3+}$, that a two-parameter equation would suffice.

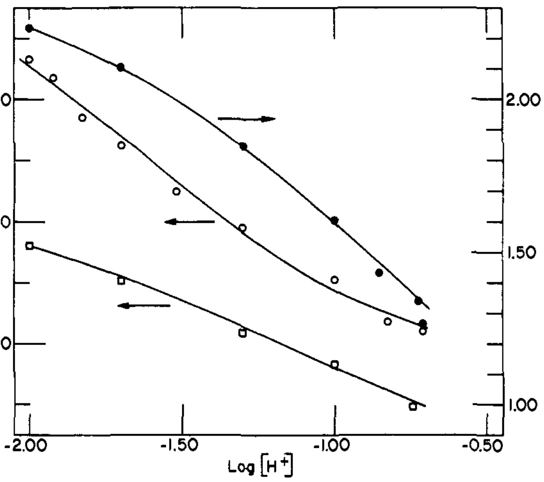

Figure 3. The pH dependence of the reaction of certain complexes with U^{3+} illustrated by a plot of log k_2 *vs.* log $[H^+]$. $Co(NH_3)_5H_2O^{3+}$ (left ordinate scale, $n = 1$, ○), *cis*-$Co(NH_3)_4(H_2O)_2{}^{3+}$ (left ordinate scale, $n = 0$, □), *trans*-$Co(en)_2(NH_3)(H_2O)^{3+}$ (right ordinate scale, $n = 0$, ●). The solid lines correspond to the least-squares fit of the rate constants to eq 4, with the resulting parameters as in Table III.

A single rate expression was sought that would correlate the data for all three complexes and represent a reasonable mechanistic proposal. (It is recognized that, for a given complex, all three of the parameters might not be needed). The following rate equation is capable of providing a good fit for all the data

$$\frac{-d[U^{3+}]}{dt} = \left(\frac{A + B[H^+]}{C + [H^+]}\right)[U^{3+}][Co(III)] \qquad (4)$$

All of the complexes do not require this complicated an expression, and none of the complexes can be studied over a really wide range of variables to confirm the parametric form of eq 4. Nevertheless, considering we have posed the logical necessity of providing a single reasonable expression and a common mechanism for all three reactions, eq 4 appears to be the best representation.

The values of parameters A, B, and C resulting from the least-squares fit of $k_{2,app}$ to eq 4 are given in Table III. The lines drawn in Figure 3 correspond to those calculated according to eq 4, and the fit is seen to be quite good for all three complexes. The mechanistic significance of this equation will be considered in the Discussion section.

Complexes Containing Reducible Ligands. Certain of the cobalt complexes studied here contain as ligands anions which are subject to reduction by U^{3+}. The reduction of the free ligand by U^{3+} does not necessarily result in ligand reduction during the reaction of RX^{2+} with U^{3+}, however, even if the ligand is utilized as the bridging group in an inner-sphere reaction. Thus $Co(NH_3)_5HC_2O_4{}^{2+}$ reacts with Cr^{2+} without reduction to glycolate or glyoxalate, whereas Cr^{2+} readily reduces free oxalic acid.[31] Ligand reduction has been noted for the reactions of $Co(NH_3)_5X^{2+}$ complexes with Cr^{2+} and other reducing agents for X = NO_3^-, NO_2^-, and ONO^-.[32–34]

All of these free anions reacted with U^{3+} rather rapidly. Assuming the U^{3+}–ligand reactions follow second-order kinetics (which was not verified in any detail) the rate constants (M^{-1} sec^{-1}) are 1.6×10^6 (NO_3^-),[35] $\sim 2 \times 10^6$ (NO_2^-), and 3.8×10^4 ($H_2C_2O_4$).

The stoichiometry data referred to earlier indicate that for the complexes $RONO_2{}^{2+}$ and $RNO_2{}^{2+}$ there is extensive interference from ligand reduction. The rate constants (25°, $\mu = 0.20$ M) are 2.0×10^5 and 1.0×10^6 M^{-1} sec^{-1}, respectively. Whether or not these particular numbers are really meaningful is dubious, however, owing to the importance of ligand reduction.

Similar data on the nitrito complex $RONO^{2+}$ and on $RHC_2O_4{}^{2+}$ indicate very little ligand reduction. The second-order rate constants at 25.0°, 0.050 M H^+, $\mu = 0.200$ M are $5.9 \pm 0.1 \times 10^5$ M^{-1} sec^{-1} for $RONO^{2+}$ and $7.3 \pm 0.4 \times 10^4$ M^{-1} sec^{-1} for $RHC_2O_4{}^{2+}$. The latter value is determined at a single $[H^+]$; for this complex a dependence on $[H^+]$ is to be expected,[36] so that the reported rate constant cannot be resolved into an expression with "true" rate constants.

Temperature and Ionic-Strength Effects. The reactions of RBr^{2+} and RCl^{2+} are the only ones for which kinetic data were evaluated at other temperatures. The respective activation parameters are $\Delta H^{\ddagger} = 2.0 \pm$

(31) (a) H. J. Price and H. Taube, *Inorg. Chem.*, 7, 1 (1968); (b) R. M. Milburn and H. Taube, *J. Phys. Chem.*, **64**, 1776 (1960).

(32) R. T. M. Fraser, *J. Chem. Soc.*, 3641 (1965).

(33) T. W. Swaddle, *J. Amer. Chem. Soc.*, **89**, 4338 (1967).

(34) R. T. M. Fraser, R. N. Lee, and K. Hayden, *J. Chem. Soc. A*, 741 (1967).

(35) It should be noted that NO_3^- reacts particularly rapidly; therefore, any Co(III) preparation originally made from $Co(NO_3)_2$ is likely to be sufficiently contaminated to give falsely high rates unless it has been extensively purified. We originally encountered nitrate contamination of $[Co(NH_3)_5NCS](ClO_4)_2$. Subsequent preparations involving no nitrate salts and extensive purifications of the original material were finally in agreement. Every other cobalt(III) complex prepared from the nitrate was reconfirmed by an independent preparation in the complete absence of nitrate.

(36) (a) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965); (b) C. Hwang and A. Haim, *ibid.*, **9**, 500 (1970).

0.3 and 2.7 ± 0.5 kcal mol^{-1}, and $\Delta S^{\ddagger} = -32.7 \pm 1.1$ and -29.0 ± 1.6 cal mol^{-1} deg^{-1}.

The reaction of RBr^{2+} and U^{3+} was studied over the range $1.5 \times 10^{-3} \leq \mu \leq 0.20$ *M* in solutions containing primarily $LiClO_4$ as the added electrolyte. Figure 4 illustrates the ionic-strength dependence in a plot of log k_2 *vs.* $\mu^{1/2}$. The plot is linear below μ 0.01 *M*, the equation being

$$\log k_2 = \log (5.3 \times 10^3) + 6.1\mu^{1/2} \qquad (5)$$

The experimental slope of 6.1 is in good agreement with the theoretical Brønsted–Bjerrum slope of $2z_1z_2A$, which is $(2)(+3)(+2)(0.509) = 6.11$ for this reaction.

Discussion

The kinetic data for the $Co(NH_3)_5X^{2+}$ complexes indicate rather strongly that the reactions proceed *via* the inner-sphere mechanism. The most covenient way of considering the results is to follow the procedure of Haim,[37] which consists in subtracting the ground-state stabilities so that comparisons can be made directly among the relative energies of the transition states containing various X groups. The computations, summarized in Table IV, show that the relative stabilities of the transition state are $N_3^- \gg NCS^-$ and $F^- \gg Cl^- > Br^-$. Considering the hard-acid character of the two metal ions, these stability orders provide a good indication that the reactions proceed by the inner-sphere mechanism.[2c,36a,37–39]

Table IV. Stability of Co–U Transition States

Complex	K_X[a]	Relative stability of $[(NH_3)_5CoXU(H_2O)_n{}^{5+}]^{\ddagger}$[b]
$RN_3{}^{2+}$	830[c]	2×10^5
RF^{2+}	~25[d]	2.8×10^3
RCl^{2+}	1.11[e,f]	7.3
$RNCS^{2+}$	470[g]	1.7
RBr^{2+}	0.35[f,h]	1.00

[a] At 25°, μ 0.1–1.0 *M;* extrapolated when necessary from other conditions. [b] Relative to RBr^{2+}; these entries are $k_{RX}K_X/k_{RBr}K_{Br}$. [c] T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **8,** 1604 (1969). [d] Estimated by C. H. Langford, *ibid.*, **4,** 265 (1965). [e] H. Taube, *J. Amer. Chem. Soc.*, **82,** 524 (1960). [f] A. Haim and H. Taube, *Inorg. Chem.*, **2,** 1199 (1963). [g] R. G. Pearson and J. W. Moore, *ibid.*, **3,** 1334 (1964), as calculated by F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1968, p 165; other workers calculated $K_{SCN} = 2.7 \times 10^3$ (ref *c*, footnote 20) from the same data. [h] R. G. Yalman, *Inorg. Chem.*, **1,** 16 (1962).

The aquo complexes merit special consideration because the result is not simply the large stability difference for OH^-- *vs.* H_2O-bridged transition states, wherein a rate law $a + b[H^+]^{-1}$, with $b/a \gg 1$, would be expected.[3,40,41] Rather, the form of the hydrogen-ion dependence suggests the existence of hydroxo-bridged precursor complexes having appreciable stability. The results are similar in some respects to those found in the case of certain other aquo complexes.[23,42–44]

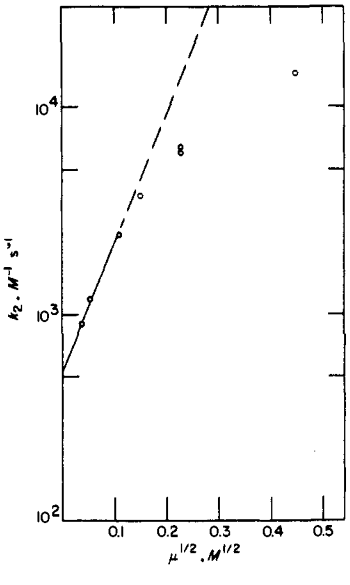

Figure 4. The ion-strength dependence of the $Co(NH_3)_5Br^{2+}$–U^{3+} reaction at 25.0° plotted as in eq 5.

It cannot be asserted that the proposed rate expression, eq 4, is established beyond question, owing to the limited range of $[H^+]$ variation which was possible and to the fact that the rate parameters assume different degrees of importance for the different complex. Nevertheless, it does seem useful to consider what this equation signifies concerning the reaction mechanism because the effect of $[H^+]$ cannot reasonably be attributed to medium effects for the reasons cited earlier.

In a case such as this the formulation of a single unique mechanism is not possible, as discussed by Newton[42,45] and by Haim.[46] Following the procedure of Newton, which has been detailed by Birk,[47] the rate law is consistent with four (and only four[48]) mechanisms comprised of steps in Scheme I. The four mechanisms leading to the same general expression consist of the combinations of reactions 1, 3, and 5; 2, 4, and 5; 1, 3, and 4; and 1, 2, and 4, the parameters *A*, *B*, and *C* being related to the individual constants.[49] Arguments might be made in favor of each of the possible mechanisms, and in view of this, as well as the questions with regard to whether eq 4 is really a well-established form, it seems not useful to detail all the considerations. Suffice it to note that the OH^--bridged

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(37) A. Haim, *Inorg. Chem.*, 7, 1475 (1968).

(38) D. L. Ball and E. L. King, *J. Amer. Chem. Soc.*, **80,** 1091 (1958).

(39) D. P. Fay and N. Sutin, *Inorg. Chem.*, **9,** 1291 (1970).

(40) D. W. Carlyle and J. H. Espenson, *J. Amer. Chem. Soc.*, **90,** 2272 (1968), and references therein.

(41) A. M. Zwickel and H. Taube, *Discuss. Faraday Soc.*, **29,** 42 (1960).

(42) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67,** 1425 (1963).

(43) M. P. Liteplo and J. F. Endicott, *J. Amer. Chem. Soc.*, **91,** 3982 (1969).

(44) R. D. Cannon and J. Gardiner, *ibid.*, **92,** 3800 (1970).

(45) T. W. Newton and F. B. Baker, *Advan. Chem. Ser.*, **No.** 71, 268 (1969).

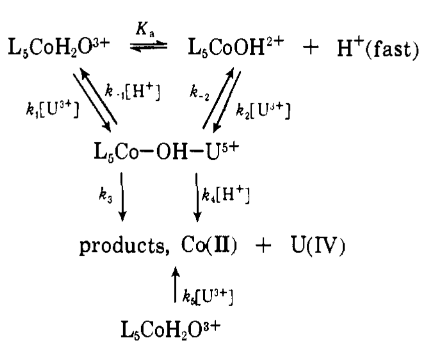
(46) A. Haim, *Inorg. Chem.*, **5,** 2081 (1966).

(47) J. P. Birk, *J. Chem. Educ.*, in press.

(48) An additional family of mechanisms can be obtained by invoking the acid dissociation of U^{3+} along with, or instead of, that of the Co(III) complex. The strong indication that, in the precursor complex and in the transition state, OH^- is a bridging ligand requires that the bridging group derive from a H_2O coordinated to Co(III) rather than to U(III), owing to the relative substitution rates.

(49) The respective mechanisms identify *A* as $k_3(k_1 + k_5)/k_{-1}$, $(k_{-2}k_{-5} + k_2k_4K_a)/k_4$, $k_1k_3/(k_{-1} + k_4)$, and $k_2K_ak_4/(k_{-1} + k_4)$; *B* as k_5, k_5, $k_1k_4/(k_{-1} + k_4)$, and $k_1k_4/(k_{-1} + k_4)$; and *C* as k_3/k_{-1}, k_{-2}/k_4, $k_3/(k_{-1} + k_4)$, and $k_{-2}/(k_{-1} + k_4)$.

Scheme I



precursor complex, $L_5Co{-}OH{-}U^{5+}$, is involved in all the possible schemes. That OH^- should form a precursor complex more stable than those of the other bridging anions may simply derive from its ability to lower the energy of the transition state during which the precursor complex reacts *via* electron transfer.

The complexes *cis*-$[Co(en)_2(H_2O)Cl^{2+}]$ and *trans*-$[Co(NH_3)_4(H_2O)CN^{2+}]$ have two potential bridging groups, the anion and OH^- from the aquo ligand. The slight acid dependence noted for these complexes may possibly represent parallel X^- and OH^- pathways, the latter perhaps related to steps in Scheme I.

The results for the aquoammine complexes of Co(III) can be compared with the very strong margin by which the OH^--bridged transition state is favored over the halide-bridged transition state in the $Cr(H_2O)_5X^{2+}$ complexes;[50] in the Cr(III) reactions, however, no kinetic evidence was obtained for a precursor complex.

The complexes $Co(NH_3)_6{}^{3+}$ and $Co(en)_3{}^{3+}$ react by outer-sphere mechanisms. The effect of anions is quite marked, as is generally the case for outer-sphere reactions.[51,52] This contrasts to the much smaller effect on inner-sphere mechanisms as noted here for the RX^{2+}–U^{3+} reactions as well as in related cases.[53] The outer-sphere activated complexes are stabilized by the various anions to markedly different extents, with F^- and NCS^- being exceptional in their ability to promote rapid electron transfer. This might be attributed to the very rapid reduction of UF^{2+} and $UNCS^{2+}$ complexes by $Co(NH_3)_6{}^{3+}$, or to the success of these anions in promoting the "pseudo-inner-sphere" reactions noted with the related Yb^{2+} reactions.[52]

It proved possible to measure the rate constants for certain complexes of the type $Co(NH_3)_5X^{2+}$, namely $X = N_3^-$, $HC_2O_4^-$, and ONO^-, even though X^- reacts with U^{3+}. The rate constants for Co(III) and X^- reduction prove to be similar, so that under conditions where $[Co(III)] \gg [U^{3+}]$, [Co(III)] was also large relative to $[X^-]$, and reduction of X^- was largely ineffective. On the other hand, the cases where $X = ONO_2^-$ and NO_2^- were interferred with by ligand reduction. We can consider two cases, with X^- reduced in a step following Co(III)–U(III) electron transfer, or with direct reduction of the ligand by U^{3+} while in the coordination sphere of Co(III). The arguments based on relative rates suggest that the first scheme cannot account for the reduction of nitrite in $RNO_2{}^{2+}$ considering the results in the nitrito complex.

Acknowledgment. We are grateful to Dr. T. W. Newton (Los Alamos Scientific Laboratory) and Professor J. P. Birk (University of Pennsylvania) for their helpful comments.

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(50) R. T. Wang and J. H. Espenson, *J. Amer. Chem. Soc.*, in press. A preliminary report on some of the CrX^{2+}–U^{3+} rates has been published (ref 5).

(51) A. M. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, **83**, 793 (1961).

(52) R. J. Christensen and J. H. Espenson, *Chem. Commun.*, 756 (1970).

(53) D. E. Pennington and A. Haim, *Inorg. Chem.*, **6**, 2137 (1967); 7, 1659 (1968).