Kinetic Studies of the Reduction of Chromium(III) Complexes by Uranium(III) Ions[1a]

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Abstract: Rates have been measured for the reaction of a series of $Cr^{III}(H_2O)_5X$ complexes by U^{3+}, for X = H_2O, F, Cl, Br, –NCS, N_3, and –SCN. The reactions follow second-order kinetics, with the apparent rate constant markedly dependent upon $[H^+]$, as in the general equation $-d[Cr(III)]/dt = d[U^{4+}]/dt = k' + k'[H^+]^{-1} + k''\cdot[H^+]^{-2}$, where different terms are appropriate for different X groups. The mechanism proposed is an inner-sphere electron transfer, in which OH^- plays the role of an especially favorable bridging group.

Very little aqueous chemistry of the strongly reducing hydrated uranium(III) cation has been reported in the literature, and virtually no studies of the rates and mechanisms of its reactions have been reported until quite recently.[2–4] Based upon the standard potential of the U^{3+}/U^{4+} couple, $E^0 - 0.63$ V,[5] U^{3+} should readily reduce Cr^{3+} and its complexes.

Because Cr^{2+} is itself a good reducing agent the number of substances capable of reducing Cr(III) complexes is rather limited. Until recently, the only reduction which had been studied was the Cr(III)–Cr^{2+} exchange reaction[6–13] and related catalytic processes.[14–20]

Partial reduction of Cr(III) has been accomplished by Eu^{2+},[21] and the very powerful reducing agent Yb^{2+} ($E^0 - 1.15$ V) readily reacts with Cr(III) complexes.[22] In addition, the catalytic effect of V^{2+} on the dissociation of CrX^{2+} complexes[13,23,24] is the consequence of initial reduction to Cr^{2+}.

In many of the reactions referred to above, the mechanism can be unequivocally assigned to be an inner-sphere process in which the ligand X of the reactant complex $(H_2O)_5CrX^{2+}$ serves as a bridging group. It is transferred to the coordination sphere of the metal ion reducing agent with which CrX^{2+} is reacting. In related cases where the mechanism cannot be inferred so directly, there is circumstantial evidence that the same scheme is operative.

In still other of the examples, use is made of a different type of inner-sphere mechanism in which the bridging ligand is derived from a coordinated water molecule of the $Cr(H_2O)_5X^{2+}$ complex *via* the equilibrium

$$(H_2O)_5CrX^{2+} \rightleftharpoons (H_2O)_4Cr(OH)X^+ + H^+ \qquad (I)$$

One system typifying both pathways is the reaction between $Cr(H_2O)_5Cl^{2+}$ and Cr^{2+} which occurs by two pathways

$$(H_2O)_5CrCl^{2+} + \overset{*}{C}r^{2+} \xrightarrow{k_{ex}} [(H_2O)_5Cr\text{–}Cl\text{–}\overset{*}{C}r(OH_2)_5{}^{4+}]^{\ddagger} \longrightarrow Cr^{2+} + \overset{*}{C}r(H_2O)_5Cl^{2+} \qquad (II)$$

$$(H_2O)_5CrCl^{2+} + \overset{*}{C}r^{2+} \xrightarrow{k_{cat}} [(H_2O)_4ClCr\text{–}\overset{H}{O}\text{–}\overset{*}{C}r(OH_2)_5{}^{3+}]^{\ddagger} + H^+ \searrow Cr^{2+} + Cl^- + \overset{*}{C}r(H_2O)_6{}^{3+} \qquad (III)$$

In the particular case referred to the reactions are distinguishable because the first[6,8] yields the same products (electron exchange), whereas the second[16,17] represents the catalysis of Cr(III) substitution. Actually the first is very much faster in the example given, $k_{ex}/k_{cat} \sim 10^4$ at $[H^+] = 1$ *M*. These reactions demonstrate that both Cl^- and OH^- are efficient bridging groups for electron transfer. The latter is present only at very low concentrations, however, because $(H_2O)_5CrCl^{2+}$ is a weak acid ($pK_a \sim 6$).

In the present work we have studied the kinetics of reduction of Cr(III) complexes by U^{3+}, as in the example

$$(H_2O)_5CrX^{2+} + U^{3+}{}_{aq} \longrightarrow Cr^{2+}{}_{aq} + U^{4+}{}_{aq} + X^- \qquad (IV)$$

Aside from investigating the neglected reactions of $U^{3+}{}_{aq}$, we are interested in establishing the mechanism of the electron transfer reaction to decide if X^- and/or OH^- is a bridging group, and to evaluate their relative efficiencies for such a process. For the Cr^{2+}–Cr(III) reactions the "product criterion" directly settles the question of a bridged transition state and the roles of X^- and OH^-. In the present cases, however, we must rely on indirect arguments based on the form of kinetic expressions and relative rates, because the ligand equilibration processes for the product U^{4+} occur too rapidly.

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(1) (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission, Contribution No. 2813; (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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Table I. Stoichiometry Experiments

Complex	$10^3[U^{3+}]_0$, *M*	$10^3[Cr(III)]_0$, *M*	$10^3[Cr^{2+}]_\infty$, *M*	$[Cr^{2+}]_\infty/[U^{3+}]_0$
$Cr(H_2O)_6^{3+}$	5.14	28.2	5.40 ± 0.03	1.05
$Cr(H_2O)_6^{3+}$	2.57	28.2	2.54 ± 0.01	0.99
trans-$CrCl_2^+$	5.14	22.5	5.40 ± 0.10	1.05

Experimental Section

Materials. Uranium(III) solutions[3] were prepared shortly before use by reduction of $U(ClO_4)_4$ or $UO_2(ClO_4)_2$ solutions with amalgamated zinc under an oxygen-free atmosphere. Conversion to U^{3+} was essentially quantitative, but each solution was analyzed by reaction with an excess of $Co(NH_3)_5Br^{2+}$. The air sensitive solutions were transferred with carefully purged and prerinsed syringes with Teflon needles.

$Cr(H_2O)_6(ClO_4)_3$ was prepared by the reaction of chromium trioxide and hydrogen peroxide in aqueous perchlorate; after decomposing the excess peroxide the compound was recrystallized twice from water. It was a solution of the doubly recrystallized salt that was used in the preparation of some of the CrX^{2+} complexes.

Solutions of *trans*-$CrCl_2^+$ in dilute $HClO_4$ were prepared from the commercial reagent grade compound $CrCl_3 \cdot 6H_2O$ which consists of *trans*-$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$,[25a,b] and were purified by cation-exchange chromatography.[25c] The cis isomer was prepared and purified by the published method;[25c] its spectrum agreed closely with the literature values and only fractions having $\epsilon_{450}/\epsilon_{635} \geq 1.44$ were used in the kinetic studies.

Solutions of $CrCl_3 \cdot 6H_2O$ were treated with a small amount of Cr^{2+} solution to generate $CrCl^{2+}$.[14,17] The bromo complex was prepared from the reaction of chromium(II) and bromine, as described by Guthrie and King,[26] and the isothiocyanate, azido, and fluoro complexes by anation procedures as described by King and coworkers.[8,27] These complexes were separated and purified by cation-exchange chromatography on a column of Dowex 50W-X8 resin. The column was first rinsed thoroughly with 0.01 and/or 0.1 *F* perchloric acid, then with 1 *F* acid which eluted the desired complex.

The unstable, S-bonded form of the monothiocyanato complex was prepared by the reaction of Cr^{2+} with a Fe^{3+} solution containing thiocyanate ions according to the procedure of Orhanović and Sutin.[28] The mixture of $CrSCN^{2+}$ and $CrNCS^{2+}$, in *ca.* 3:1 ratio, was obtained by ion exchange, and analyzed for its $CrSCN^{2+}$ content by the V^{2+} procedure these authors described.[28] This solution was used directly for the U^{3+}–$CrSCN^{2+}$ kinetic studies. The other component, $CrNCS^{2+}$, reacts with U^{3+} much more slowly, and caused no interference by its presence.

The stock solution of each chromium(III) complex was analyzed for chromium spectrophotometrically after oxidation to chromate in alkaline solution with hydrogen peroxide (ϵ_{372} 4.84 × 10^3 M^{-1} cm^{-1}). The visible-uv spectrum of each complex was determined, and the molar absorptivities were calculated on the basis of the analysis for total chromium;[29] in every case good agreement with the literature values was noted.

Solutions of the Cr(III) complexes were frozen and stored at −78° until use, which proved quite effective in preventing decomposition. Other reagents were prepared as before.[30] Conductivity water was used throughout the preparative and kinetic procedures.

Kinetic Studies. Most of the reactions were followed using a Cary Model 14 recording spectrophotometer with a water-filled thermostated cell holder. The faster reaction of $CrSCN^{2+}$ was followed using a stopped-flow instrument of the design of Dulz and Sutin,[31] which has been described earlier.[32]

All the kinetic studies were carried out at 25.0° and at an ionic strength of 0.200 *M* maintained by the addition of lithium perchlorate. In most runs the absorbance was followed at the λ 350-nm peak of U^{3+} (ϵ 1.58 × 10^3 M^{-1} cm^{-1}), but some runs were carried out at other wavelengths. Typical reaction times were 2–40 min, so that the aquation of the Cr(III) complexes was not significant during the times required to prepare the solution and carry out the rate experiment.

In all of the experiments, except for the $CrSCN^{2+}$ reactions, Cr(III) was in at least tenfold excess over $[U^{3+}]_0$. Pseudo-first-order rate plots were constructed from the recording of absorbance, *D*, as a function of time, making use of a plot of log $(D - D_\infty)$ *vs.* *t* and/or a plot based on the Guggenheim method,[33] of log $(D_t - D_{t+\tau})$ *vs.* *t*, with τ = two to three half-lives. The reaction of $CrSCN^{2+}$ with U^{3+} had reversed concentrations: U^{3+} was in ≥tenfold excess. In both instances the first-order rate plots were linear for two or more half-times. The rate constants were assumed to follow a second-order rate law

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

and the value of k_2 in each run was computed from the pseudo-first-order rate constant and the average concentration of the excess reagent. At most (77%) concentrations the rate determinations were carried out in duplicate.

Results

Stoichiometry. In two of the reactions, with $Cr(H_2O)_6^{3+}$ and *trans*-$Cr(H_2O)_4Cl_2^+$, experiments were carried out to verify the 1:1 stoichiometry written in reaction IV. The Cr^{2+} produced was analyzed by adding an excess of $Co(NH_3)_5Br^{2+}$ to the completed reaction solution. The decrease in concentration of the Co(III) complex was analyzed at its peak at λ 253 nm as described earlier.

The results of these stoichiometry experiments are given in Table I.

The reaction appears to proceed essentially quantitatively in accord with reaction IV. What deviations there are may possibly arise from air oxidation of U^{3+} during the syringe transfer procedure.

Kinetics. All of the reactions of Cr(III) complexes followed the second-order rate expression given by eq 1, the value of k_2 being independent of the starting concentration of U^{3+} or of the Cr(III) complex at any particular $[H^+]$. The rate constants for each of the individual rate experiments are summarized elsewhere.[29]

For every complex the apparent second-order rate constant decreases with increasing $[H^+]$, which was varied from 0.01 to 0.20 *M* for each reaction. The different reactions showed different degrees of sensitivity to $[H^+]$, however, from Cr^{3+} at one extreme to $CrSCN^{2+}$ at the other. A general equation correlating all the ob-

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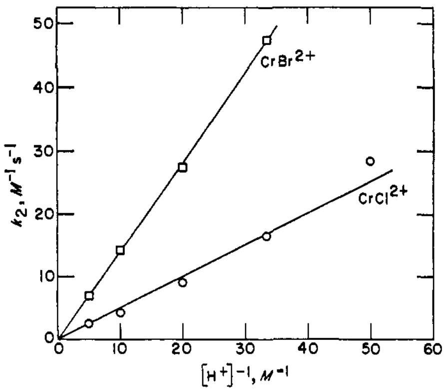

Figure 1. The variation with $[H^+]$ of the apparent second-order rate constants for $CrCl^{2+}$ and $CrBr^{2+}$ according to the equation $k_2 = b[H^+]^{-1}$.

servations is given by

$$k_2 = a + b[H^+]^{-1} + c[H^+]^{-2} \tag{2}$$

where for any particular complex one or two of the empirical parameters is within experimental error of zero.

The results for $CrCl^{2+}$ and $CrBr^{2+}$ are depicted in Figure 1 by a plot of k_2 *vs.* $[H^+]^{-1}$, which establishes that the b term is the major term for this pair of complexes, and possibly the only term of importance.[34] A similar plot is shown in Figure 2 for CrF^{2+}, CrN_3^{2+}, and both isomers of $CrCl_2^+$. These plots are also linear, but the finite intercepts indicate that the first two terms of eq 2 are needed to account for the $[H^+]$ dependence of k_2.

The two slowest reacting ions, Cr^{3+} and $CrNCS^{2+}$, also show the strongest dependence on $[H^+]$. Both reactions show terms dependent on $[H^+]^{-1}$ and $[H^+]^{-2}$ over the concentration range studied, with the last term particularly dominant for Cr^{3+}. Figure 3 presents a plot of $k_2[H^+]$ *vs.* $[H^+]^{-1}$. The plot is linear for both reactions, confirming that the last two terms of eq 2 satisfactorily describe the hydrogen ion effect.

The reaction of the unstable linkage isomer $CrSCN^{2+}$ deserves special comment. First of all, this complex reacts considerably more rapidly than other complexes. Although the data are rather imprecise, the effect of changing $[H^+]$ is much less than in the other cases. Owing to the poor precision, the parameters of eq 2 are not accurately evaluated; we approximate $a = 8.5 \pm 0.5 \times 10^3\ M^{-1}\ \text{sec}^{-1}$ and $b = 20 \pm 40\ \text{sec}^{-1}$. The reality of the b term cannot be affirmed from the present data.

We note a dramatic catalytic effect of free SCN^- on the rate constants for $CrSCN^{2+}$, which is consistent with the equation

$$k_2 = 9 \times 10^3 + 1.9 \times 10^5[SCN^-] \tag{3}$$

In the absence of added SCN^-, the reactant concentrations are such that the amount of SCN^- released as reaction IV proceeds is much smaller than that added in these anion catalysis experiments, however. Consequently, there is no reason to expect any acceleration accompanying the formation of SCN^- as the reaction proceeds and none was observed; the pseudo-first-order plots remain quite linear.

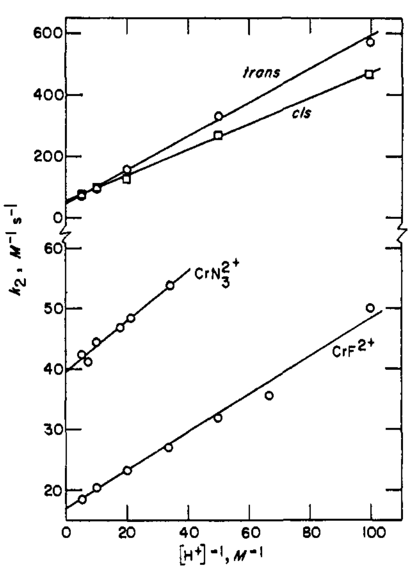

Figure 2. The variation with $[H^+]$ of the apparent rate constants for CrF^{2+}, CrN_3^{2+}, and *cis*- and *trans*-$CrCl_2^+$ according to the equation $k_2 = a + b[H^+]^{-1}$.

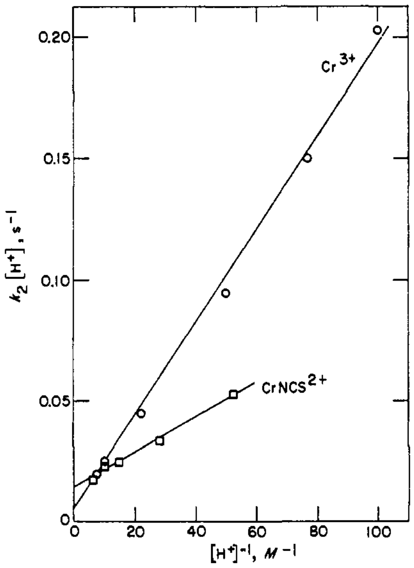

Figure 3. The variation with $[H^+]$ of the apparent second-order rate constants for Cr^{3+} and $CrNCS^{2+}$ according to the equation $k_2 = b[H^+]^{-1} + c[H^+]^{-2}$.

Table II summarizes the rate parameters, based on eq 2, which describe the fit of the data for each complex to that relation, using just those terms that are appropriate for that particular reaction.

Interpretation and Discussion

The most prominent feature of the kinetics of the present reaction is the strong reciprocal dependence on $[H^+]$. Using $CrCl^{2+}$ as an example, the information at the most strictly interpreted level reveals only the form of the net activation process,[35] which is given by (V) for the pathway represented by b and makes no specifica-

$$CrCl^{2+} + U^{3+} + H_2O \longrightarrow [Cr,U,Cl,OH^{4+}]^{\ddagger} + H^+ \tag{V}$$

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[34] A statistical analysis of the $CrCl^{2+}$ data according to eq 2 with a and/or c terms included (a, b; b, c; a, b, c) gives values of b within two standard deviations of the value found when only the b term was employed in the fit. The resulting values of a and c are small, usually within three standard deviations of zero.

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Table II. Rate Parameters for the Cr(III)–U(III) Reactions[a,b]

Complex	a, M^{-1} sec^{-1}	b, sec^{-1}	c, M sec^{-1}
$CrBr^{2+}$		1.42	
$CrCl^{2+}$		0.48	
CrF^{2+}	17	0.31	
CrN_3^{2+}	40	0.41	
$CrSCN^{2+}$	~9000	(0)[c]	
trans-$CrCl_2^+$ [d]	44	5.5	
cis-$CrCl_2^+$ [e]	51	4.3_5	
Cr^{3+}		0.006	0.00187
$CrNCS^{2+}$		0.014	0.00074
$Cr(NH_3)_5Cl^{2+}$	~0.008		

[a] According to eq 2; 25.0°; $\mu = 0.200$ *M*. [b] A missing entry indicates that that rate term was of negligible importance over the range of $[H^+]$ studied in these experiments. 0.01–0.20 *M*. [c] The value of b for $CrSCN^{2+}$ is quite uncertain; $a = 8500$, $b = 40$, constitutes an equally good description of the data. [d] Corrected as described in the text, for the reaction of *trans*-$CrCl_2^+$ with Cr^{2+}; the rate constant for *trans*-$CrCl_2^+$ is $45 + 5.6/[H^+]$. [e] Corrected as described in the text, for the reaction of *cis*-$CrCl_2^+$ and Cr^{2+}; the rate constant for *cis*-$CrCl_2^+$ is $63 \times 4.2/[H^+]$.

tion as to whether it is a Cr(III) or a U(III) water molecule that undergoes the requisite dissociation.

In contrast to the strongly $[H^+]$-dependent rates of $(H_2O)_5CrX^{2+}$ reduction, no rate dependence on $[H^+]$ is noted[3] for complexes such as $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_6^{3+}$ which contain no such acidic protons. In addition, a few experiments were carried out on the reduction of $Cr(NH_3)_5Cl^{2+}$ by U^{3+}. This reaction occurs quite slowly, and the experiments are rather difficult, but the rate does not seem to depend upon $[H^+]$. These facts considered, it seems reasonable that the hydroxo group in reaction V derives from the coordination sphere of Cr(III), and not from that of U(III), suggesting the two-step mechanism

$$(H_2O)_5CrCl^{2+} \rightleftharpoons (H_2O)_4Cr(OH)Cl^+ + H^+ \quad K_a \qquad (I)$$

$$(H_2O)_4Cr(OH)Cl^+ + U^{3+} \longrightarrow [\ldots{}^{4+}]^{\ddagger} \longrightarrow U(IV) + Cr(II) \quad k_1 \qquad (VI)$$

according to which $b = K_ak_1$.

In order to make reaction VI believable as an elementary reaction, some explanation is needed for why it predominates to such a large extent over the parallel process (reaction VII) in which the transition state contains an additional proton, and which might have been anticipated as the more important.

$$(H_2O)_5CrCl^{2+} + U^{3+} \longrightarrow [\ldots{}^{5+}]^{\ddagger} \longrightarrow U(IV) + Cr(II) \qquad (VII)$$

In this context, we note that the role of OH^- is almost certainly not an incidental one, such as a nonbridging ligand on Cr(III), because precedent for that type of mechanism is not found in any of the redox reactions of $CrCl^{2+}$. Whenever an inverse dependence on $[H^+]$ has been noted, as in reaction III, the OH^- has functioned as a bridging group for electron transfer.

These results lead us to conclude that OH^- acts as a bridging group in all of the $[Cr,U,X,OH]^{\ddagger}$ transition states. The functioning of OH^- in such a capacity is equivalent to the inequality $k_1 \gg a$, because K_a is a very small number.[36] The involvement of OH^- as a bridging group does not preclude the possibility that X^-, itself a good bridging group, simultaneously acts as a bridging group. Precedent for doubly bridged OH^-, X^- transition states is to be found in the electron exchange reactions of CrX^{2+} and Cr^{2+}, where in two cases, namely $X = H_2PO_2^-$ and OAc^-,[13] the rate expression is $k_{ex}[CrX^{2+}][Cr^{2+}][H^+]^{-1}$, and the transition state with bridging X^- and OH^- in cis positions is involved. The reaction of $CrCl^{2+}$ with V^{2+} [28] follows the rate law $k_2 = a + b[H^+]^{-1}$, and the second term may correspond to a doubly bridged transition state.

In support of the double-bridged transition state, it is noted that the reductions of $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5NCS^{2+}$ are the reactions which proceed slowly, and which make use of a transition state containing two OH^-'s. The presence of only inefficient bridging groups (H_2O, NCS^-) suggests that in such cases the proclivity toward double bridging manifests itself as the $[H^+]^{-2}$ rate dependence.

In those complexes where the bridging group is a good one, *e.g.*, CrF^{2+} and CrN_3^{2+}, and particularly $CrSCN^{2+}$, a substantial contribution from a $[H^+]$-independent pathway is noted. Two alternatives, which at present we are unable to distinguish, should be mentioned. The term $a[CrX^{2+}][U^{3+}]$ might arise simply from the role of X^- as a singly bridged anion competing with the OH^- form because these are good bridging ligands. Alternatively, this reaction pathway, as that with a $[H^+]^{-1}$ dependence, may utilize OH^- as a bridging group, with a simultaneous protonation of the departing X^-, as $[HXCrOHU^{5+}]^{\ddagger}$.

The experiments with the isomeric forms of $CrCl_2^+$ were carried out to examine some of the factors controlling the use of OH^- and X^- bridging groups. The two complexes react nearly identically, and although it is unwarranted to base firm conclusions on small rate differences at a single temepratures, we are naturally led to believe that the mechanisms are closely related. A rate term independent of $[H^+]$ was noted for each complex, in contrast to $CrCl^{2+}$. It should also be noted that the lower charge on the dichloro complexes may account for the less dominant role of the hydroxo pathway here.

Aside from questions relating to the structures of the specific hydroxo-containing transition states, the question must be raised as to why they so dominate the reductions of Cr(III) complexes, in view of the presence of ligands, such as halide ions, that are known to be good bridging ligands. The explanation we offer is that they stabilize the transition state to an exceptional extent because the incipient U^{4+} ion is highly acidic, and hard bases, such as OH^-, serve to add to its stability, thereby promoting the reaction. For that to be the case, the OH^- group must reside in the primary coordination sphere of uranium in the transition state. As pointed out earlier, however, the OH^- group is reasonably accounted for only if it is a bridging ligand. This rules out of consideration a transition state $[Cr\text{–}X\text{–}U\text{–}OH^{4+}]^{\ddagger}$. The very low rate at which the Cr(III) complexes exchange water molecules with the bulk solvent requires that the OH^- group originate by dissociation of a water molecule coordinated to Cr(III).

The favorable role played by OH^- as a bridging group in the present reactions may be compared to what is found[2] for the reduction of aquoammine Co(III) complexes.[3] These reactions involve a precursor complex of appreciable stability, $[(NH_3)_5Co\text{–}OH\text{–}U^{4+}]$, for example. If the present reactions involve a similar intermediate, its stability and reactivity cannot be separately evaluated from the kinetic measurements.

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(36) K_a for the CrX^{2+} ions is of the order of 10^{-6} *M* [N. Bjerrum, *Z. Phys. Chem.*, 59, 336 (1907)] and is 1.1×10^{-4} *M* for Cr^{3+}: C. Postmus and E. L. King, *J. Phys. Chem.*, 59, 1208 (1955).

An interesting comparison can be made between the reduction of Cr^{3+} by U^{3+} and the oxidation of Cr^{2+} by Np^{4+}, studied by Thompson and Sullivan.[37]

$$Cr^{3+} + U^{3+} = Cr^{2+} + U^{4+}$$

$$Cr^{2+} + Np^{4+} = Cr^{3+} + Np^{3+}$$

These authors find a rate expression identical with that in eq 2, with a negligible $[H^+]$-independent term. The two important transition states are, therefore, $[Cr \cdot OH \cdot Np^{5+}]^{\ddagger}$ and $[Cr \cdot (OH)_2 \cdot Np^{4+}]^{\ddagger}$. The very close correspondence of the mechanisms for U and Np should be noted.

An informative comparison of the reactivity of the different Cr(III) complexes can be carried out, based on the approach suggested by Haim.[38] One must correct for the differing stabilities of the individual CrX^{2+} equilibria

$$Cr^{3+} + X^- \rightleftharpoons CrX^{2+} \qquad K_X \qquad \text{(VIII)}$$

so that the comparisons will, in fact, refer to the inherent stability of the transition states.

The computations, summarized in Table III, indicate that the transition states containing F^- and N_3^- are, relatively, the most stable, whether they refer to the term $a[CrX^{2+}][U^{3+}]$ or $b[CrX^{2+}][U^{3+}][H^+]^{-1}$. The former is to be expected,[36] because the metal ions are both quite hard acids. The corresponding effects of the same anions in stabilizing the hydroxo-bridged transition states may be cited as supporting evidence in favor of the doubly bridged (OH^-, X^-) formulation, as opposed to OH^- bridging alone, in which case the various nonbridging X^-'s would be expected to exert less pronounced effects.

Table III. Stability of Cr–U Transition States

Complex	K_X,[a] M^{-1}	Relative[b] stability of $[Cr,X,OH,U^{4+}]^{\ddagger}$	Relative[c] stability of $[Cr,X,U^{5+}]^{\ddagger}$
CrF^{2+}	1.7×10^4 [d]	1.6×10^6	*ca.* 2×10^3
CrN_3^{2+}	*ca.* 1×10^3 [e]	*ca.* 1.3×10^5	*ca.* 8×10^3
$CrNCS^{2+}$	1.7×10^2 [f]	7.7×10^2	±0.6
$CrCl^{2+}$	8×10^{-2} [g]	13	
$CrSCN^{2+}$	7×10^{-4} [h]	0–10[i]	*ca.* 1.0
$CrBr^{2+}$	2.2×10^{-3} [j]	1.0	

[a] At 25°, extrapolated when necessary from other conditions. [b] Relative to $CrBr^{2+}$. [c] Relative to $CrSCN^{2+}$. [d] Reference 27b. [e] Estimated from data on FeN_3^{2+} and VN_3^{2+}: ref 32 and J. H. Espenson and J. R. Pladziewicz, *Inorg. Chem.*, **9**, 1380 (1970). [f] C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955). [g] R. J. Baltisberger and E. L. King, *J. Amer. Chem. Soc.*, **86**, 795 (1964). C. F. Hale and E. L. King, *J. Phys. Chem.*, **71**, 1779 (1967). [h] Estimated, ref 24. [i] The value of parameter *b* for $CrSCN^{2+}$ is quite uncertain. [j] J. H. Espenson and E. L. King, *J. Phys. Chem.*, **64**, 380 (1960); $\mu = 2.0\ M$.

The ratio of CrN_3^{2+} and $CrNCS^{2+}$ reactivity is 29 along path *b*, corresponding to the transition state $[Cr,X,OH,U^{4+}]^{\ddagger}$. Since both transition states are promoted by the bridging OH^-, the lessened rate discrimination between N_3^- and NCS^- should not be taken as evidence for X being in a nonbridging position in the transition states. The estimated value of *a* for the $CrNCS^{2+}$ reaction is $\leq 0.02\ M^{-1}\ sec^{-1}$. The reactivity ratio for that pathway is therefore $a(N_3^-)/a(NCS^-) \geq 2 \times 10^3$, which provides confirming evidence[39] for bridging azide and thiocyanate ions in the $[H^+]$-independent pathway.

Finally, a question must be raised concerning the apparent simplicity of the $CrCl_2^+$ reactions, which for the trans isomer was shown to proceed according to the equation

$$CrCl_2^+ + U^{3+} \longrightarrow Cr^{2+} + U^{4+} + 2Cl^- \qquad k_1 \qquad \text{(IX)}$$

with $k_1\ (M^{-1}\ sec^{-1}) = 44 + 5.5[H^+]^{-1}$ for the trans isomer, and $k_1 = 51 + 4.35[H^+]^{-1}$ for the cis (25.0°, $\mu = 0.200\ M$).

The complication arises because of the known reactions

$$CrCl_2^+ + Cr^{2+} \longrightarrow CrCl^{2+} + Cr^{2+} + Cl^- \qquad k_2 \qquad \text{(X)}$$

for which $k_2\ (M^{-1}\ sec^{-1}) = 400$ for trans, and $k_2 = 288$ for cis, independent of $[H^+]$ (25.0°, $\mu = 1.0\ M$).[14] If (X) occurs to any substantial extent, then the following also may become important.

$$CrCl^{2+} + U^{3+} \longrightarrow Cr^{2+} + U^{4+} + Cl^- \qquad k_3 \qquad \text{(XI)}$$

for which $k_3\ (M^{-1}\ sec^{-1}) = 0.52[H^+]^{-1}$ (25.0°, $\mu = 0.200\ M$, Table III).

The effect of these side reactions was estimated using a numerical solution[40] to the simultaneous differential equations. When k_1 is large, as in the runs with low $[H^+]$ and with the higher concentrations of $CrCl_2^+$, reaction X causes a trivial effect. At high $[H^+]$ and low $[CrCl_2^+]$, the effect is more appreciable, in a direction that, ignoring the side reactions, would obtain an experimental rate constant for reaction IX lower than the true value. For the actual experiments performed, the corrections averaged 2.4% (trans) and 4.8% (cis), with a maximum individual correction of 8.4%. The data shown in Figure 2 are the uncorrected values. After correction the rate constants are $k_1 = 45 + 5.6 \cdot [H^+]^{-1}$ for *trans*-$CrCl_2^+$ and $63 + 4.2[H^+]^{-1}$ for cis. Reaction X was responsible for the entire correction, reaction XI being of negligible importance.

The effect of anions on other U^{3+} reactions has been noted, especially in the outer-sphere reactions of $Co(NH_3)_6^{3+}$.[3] The effect of SCN^- on the reaction of U^{3+} and $CrSCN^{2+}$ was not studied thoroughly, but it appears that U(III) thiocyanate complexes are more reactive than the hydrated cation. A more quantitative consideration must await experiments on the rates and equilibria of the U(III)–SCN^- system.

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(40) The computer program used for solving the differential rate equations was that employed in similar situations [ref 23 and J. H Espenson and L. A. Krug, *ibid.*, **8**, 2633 (1969)], with the differential equations and stoichiometry appropriate to the present case.