A mechanism consistent with the molecularity of the reaction is

$$AnO_2^{2+} + I^- = AnO_2^+ + I^0 \qquad (6)$$

as the rate-determining step. The recombination and equilibrium reactions that generate the product I_3^- which would follow eq 6 are assumed to be rapid. The data presented do not provide direct evidence for the participation of a radical I^0 species in the reaction scheme. It should be noted, however, that the thermodynamic properties of this radical, estimated by Margerum,[9] provide no criteria which eliminate the possibility of the proposed mechanism.

If we assume that the reactions between the AnO_2^{2+} and I^- ions proceed solely by outer-sphere transition states and that the other relevant criteria are satisfied, it is of interest to compare these reactions in terms of the Marcus cross relations.[4] The results of such calculations[10] [k_{obsd} (M^{-1} s^{-1}), k_{calcd} (M^{-1}, s^{-1})] are as follows, for the oxidants Np(VI), Pu(VI), and Am(VI) at 25 °C, respectively: 530, 2 × 10^3; 17, 8; >3 × 10^6, 1 × 10^7. The agreement between calculated and observed values of the rate constants is adequate and provides a reasonable description of the variation in ΔG^* with change in ΔG^0 for a series of closely related reactions.

It is of interest to note that the differences in the rates of reduction of Np(VI) and Pu(VI) by I^- are governed by differences in ΔH^*. This feature has not been previously observed for reactions of Np(VI) and Am(VI) with common reductants,[11,12] similar systems where a priori considerations would

dictate that there be no significant variation in the respective values of ΔS^*. The extension of the Marcus formalism[4] to calculations of ΔH^* and ΔS^* offers no apparent rationalization of these observatons.

References and Notes

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(8) The functional form is $k_{obsd} = 2kT/h \exp(-\Delta H^*/RT) \exp(\Delta S^*/R)[I^-] \cdot \exp(a[I^-])$. We thank Dr. E. A. Deutsch, University of Cinncinnati, for his computational assistance.
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Kinetics and Mechanisms of the Reductions of Thallium(III) and Chromium(III) by Uranium(III) in Perchlorate Media

A. EKSTROM,* A. B. McLAREN, and L. E. SMYTHE

The kinetics and mechanisms of the reaction of U(III) with Tl(III) and Cr(III) have been examined in perchlorate media. The Tl(III) reaction was found to obey the rate law $-d[U(III)]/dt = [U^{3+}][Tl^{3+}]\{k_{-1}K/(H + K)\}$ in which k_{-1} has a value of $(3.6 \pm 0.2) \times 10^5$ M^{-1} s^{-1} at 20 °C and an ionic strength of 2.0 M, whereas the Cr(III) reaction was found to exhibit a mechanism dominated by a reaction path having an inverse second-order acid concentration dependence. The rate constants are compared with those obtained for other similar systems; it is suggested, that the acid concentration independent and the inverse acid concentration dependent reaction paths of many electron-transfer reactions involving metal ions exhibit a limiting rate of 10^6–10^7 M^{-1} s^{-1}. Plausible reasons for this limiting value are discussed.

Introduction

Uranium(III) is a sufficiently powerful reducing agent to reduce a wide variety of metal ions at measurable rates, thus making it an ideal reagent for comparative studies. Detailed examinations of the kinetics and mechanisms of reactions of U(III) with Fe(III), V(IV), V(III),[1] Co(III),[2] and several aquoamine complexes of Co(III)[3] have been reported, and this paper extends these studies to the reduction of Tl(III) and to the determination of the activation parameters of the U(III)–Cr(III) reaction for which the rate law had been previously reported.[4] Tl(III) and Cr(III) were chosen for study because both are extensively hydrolyzed in aqueous solution, and the participation of hydrolyzed species in the rate law was expected, thus providing further data necessary to permit comparisons of the rate constants and rate parameters of the

acid-independent and acid-dependent reaction paths for the reactions of the U(III) ion.

Experimental Section

Solutions of U(III)[1] and Cr(III)[4] were prepared and analyzed as described previously. U(IV) solutions were obtained by passing oxygen through U(III) solutions and purging with argon gas. A stock solution of Tl(ClO$_4$)$_3$ was prepared by dissolving analytical reagent grade Tl$_2$O$_3$ (Merck) in 9 M HClO$_4$ and analyzed by titration with standard I$_2$.[5] All solutions were purged with high-purity argon gas for at least 30 min prior to use. Kinetic measurements were made with a stopped-flow spectrophotometer and computerized data acquisition systems.[6]

Results

(a) U(III)–Tl(III) Reaction. The reaction was followed at 350 nm, where U(III) was found to be the only absorbing species, with an extinction coefficient of 1550 ± 60 M^{-1}. The

Table I. Apparent Second-Order Rate Constants at Various Initial U(III) and Tl(III) Concentrations[a]

[U-(III)]$_0$, M × 10^4	[Tl-(III)]$_0$, M × 10^4	No. of detn	$10^{-4}k_1$,[c] $M^{-1} s^{-1}$	R[b]
5.04	0.499	12	5.2 ± 0.2	1.03 ± 0.02
5.04	0.997	8	4.7 ± 0.1	1.01 ± 0.02
5.04	1.99	12	4.9 ± 0.2	1.00 ± 0.01
5.04	5.98	12	5.5 ± 0.2	
1.21	7.28	10	5.7 ± 0.2	
2.42	7.28	12	5.7 ± 0.1	
4.83	7.28	12	5.2 ± 0.1	
9.66	7.28	12	5.9 ± 0.3	
2.42	3.64	11	5.8 ± 0.3	
		101	Av 5.3 ± 0.2	

[a] $[H^+]$ = 1.00 M, μ = 2.00, 20.0 °C, 350 nm. [b] Ratio of the observed absorbance change divided by the change required by eq 1. [c] Values of k_1 are the average of the number of determinations quoted, the error being the standard deviation.

Table II. Effect of Acid Concentration and Temperature on the Rate Constant of the U(III)-Tl(III) Reaction[a]

[H-Cl-O$_4$], M	$10^{-4}k_1$, $M^{-1} s^{-1}$				
	10.1 °C	14.9 °C	20.0 °C	25.0 °C	30.0 °C
0.20	13.3 ± 0.3	18.3 ± 0.4	23.6 ± 0.6	29.6 ± 0.4	
0.40	6.6 ± 0.2	9.7 ± 0.2	12.2 ± 0.1	15.8 ± 0.4	23.4 ± 0.6
0.60	4.4 ± 0.1	6.3 ± 0.2	9.4 ± 0.1	10.6 ± 0.2	15.4 ± 0.4
0.80	3.8 ± 0.1	5.1 ± 0.1	6.9 ± 0.1	9.0 ± 0.2	12.6 ± 0.2
1.00	3.0 ± 0.1	4.2 ± 0.1	5.9 ± 0.1	7.1 ± 0.1	10.1 ± 0.1
1.50	1.99 ± 0.04	2.82 ± 0.06	4.8 ± 0.1	4.8 ± 0.1	7.0 ± 0.1
1.90			3.9 ± 0.1		

[a] [U(III)] = 3.14 × 10^{-4} M, [Tl(III)] = 3.64 × 10^{-4} M, μ = 2.00 M. Values of k_1 are the average of at least 10 determinations, the error being the standard deviation.

Table III. Calculated[a] Values of k_4 for the U(III)-Tl(III) Reaction

Temp, °C	K_2,[b] M^{-1}	$10^{-5}k_4$, $M^{-1} s^{-1}$	α	% rms[c]
10.1	0.069	4.7 ± 0.3	−0.04 ± 0.07	5.9
14.9	0.073	6.5 ± 0.2	−0.06 ± 0.04	4.2
20.0	0.076	7.2 ± 0.3	0.16 ± 0.06	6.0
25.0	0.080	9.9 ± 0.4	−0.03 ± 0.03	4.1
30.0	0.084	12.9 ± 0.4	0.02 ± 0.02	2.5

[a] Calculated from eq 4, using the data from Table II. [b] Extrapolated hydrolysis constants for Tl(III); see text. [c] Percent root-mean-square deviation; see ref 1.

spectral changes measured for the U(III)-Tl(III) reaction in the presence of excess U(III) confirmed the stoichiometry of eq 1. Plots of the integrated second-order rate law gave

$$2U(III) + Tl(III) \xrightarrow{k_1} 2U(IV) + Tl(I) \qquad (1)$$
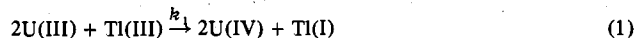
excellent straight lines to 85% reaction, and the second-order rate constants calculated from these data were essentially independent of the initial concentrations of U(III) and Tl(III) (Table I), the average of 101 runs giving a value for k_1 of (5.3

± 0.2) × 10^4 M^{-1} s^{-1} at 20 °C, $[H^+]$ = 1.0 M, and an ionic strength of 2.00 M.

U(III) was found to reduce Tl(I) to the metal if the initial U(III) concentration both was high (>10^{-2} M) and was in excess of the initial Tl(III) concentration. The rate constant of this reaction was estimated to be several orders of magnitude smaller than k_1 and no significant interference from this reaction to the determination of k_1 was found at the lower initial reagent concentrations used in this study. Nevertheless, all subsequent runs were carried out using an excess of Tl(III).

In previous studies of the reduction of Tl(III) by V(IV)[7] and Fe(II)[8] it was found that the presence of the reaction products markedly decreased the value of the observed rate constants, these observations being attributed to the presence of an inhibiting back-reaction. In the present study, the addition of U(IV) or Tl(I) in concentrations of up to 10^{-2} M was found to have no statistically significant effect on the value of k_1, thus indicating the absence of similar complicating features in the present system.

The effect of acid concentration on the value of k_1 was studied over the range 0.20-1.90 M H^+ and over the temperature range of 10.1-30.0 °C, NaClO$_4$ being used to maintain the ionic strength constant at 2.0 M. The results obtained (Table II) indicate the marked acid dependence of k_1, and plots of k_1 vs. $1/([H^+] + K_2)$ were found to be excellent straight lines passing through the origin. The inclusion of K_2, defined by eq 2,[9] was necessary because the hydrolysis constant

$$Tl^{3+} + H_2O \xrightarrow{K_2} TlOH^{2+} + H^+ \qquad (2)$$

of Tl(III) is sufficiently large[9] to make a significant contribution to the equilibrium H^+ concentrations. Accordingly, the data of Table II were analyzed using eq 3, which can be

$$k_1 = \exp\{\alpha[H^+]\}k_4K_2\{[H^+] + K_2\}^{-1} \qquad (3)$$

readily derived by combining eq 2 with the most probable rate-controlling step represented by eq 4; the exponential term

$$U^{3+} + TlOH^{2+} \xrightarrow{k_4} [U \cdot OH \cdot Tl]^{5+} \qquad (4)$$

in eq 3 represents the usual Harned correction.[10] The unknowns α and k_4 of eq 3 were obtained (Table III) by nonlinear least-squares analysis of the data in Table II, the values of K_2 at the various temperatures (Table III) being obtained by interpolation of published data.[9] As summarized in Table III, the values of α are statistically significant only at 20 °C and do not show any consistent temperature dependence. Consequently the acid and temperature dependences of k_1 (Table II) were also analyzed simultaneously without the Harned parameter to yield values of 8.0 ± 0.4 kcal mol^{-1} and −4.1 ± 1.4 cal deg mol^{-1} respectively for ΔH^* and ΔS^* of k_4 with a root-mean-square deviation (% rms) of 7.7%.

(b) U(III)-Cr(III) Reaction. It has been reported[4] that this reaction obeys a second-order rate law, that it has an observed rate constant of 0.077 M^{-1} s^{-1} at 25 °C, at $[H^+]$ = 0.20 M, and at an ionic strength of 0.20 M, and that the reaction proceeds by a combination of two reaction paths having respectively an inverse first-order and inverse second-order acid dependence. The present study, in which the reaction was

Table IV. Effect of Acid Concentration and Temperature on the Rate Constant of the U(III)-Cr(III) Reaction[a]

[HClO$_4$], M	14.9 °C	20.0 °C	22.9 °C	25.0 °C	30.1 °C
0.052	0.67 ± 0.03	1.11 ± 0.03	1.27 ± 0.04	1.70 ± 0.09	3.06 ± 0.13
0.102	0.184 ± 0.003	0.295 ± 0.001	0.340 ± 0.004	0.414 ± 0.007	0.66 ± 0.01
0.152	0.114 ± 0.001	0.159 ± 0.001	0.193 ± 0.003	0.229 ± 0.003	0.348 ± 0.007
0.202	0.079 ± 0.001	0.117 ± 0.003	0.134 ± 0.001	0.158 ± 0.003	0.230 ± 0.004
0.252	0.069 ± 0.007	0.089 ± 0.003	0.105 ± 0.001	0.121 ± 0.001	0.174 ± 0.004

[a] [U(III)] = 5.04 × 10^{-4} M, [Cr(III)] = 7.48 × 10^{-2} M, ionic strength 2.0 M. Values of k are the averages of at least eight determinations; the error being the standard deviation. Units are M^{-1} s^{-1}.

Table V. Calculated Values of k_s' and k_s'' for the U(III)–Cr(III) Reaction

| Temp, °C	$10^2 k_s'$, M^{-1} s^{-1}		$10^3 k_s''$, M^{-3} sec^{-1}	
	Detn from eq 5^a	Calcd^b	Detn from eq 5^a	Calcd^c
14.9	4.2 ± 0.5	4.1	1.6 ± 0.1	1.5
20.0	4.8 ± 0.4	5.1	2.6 ± 0.5	2.4
23.0	5.9 ± 0.3	5.7	3.0 ± 0.1	3.2
25.0	6.2 ± 0.3	6.2	3.8 ± 0.1	3.8
30.0	7.5 ± 1.4	7.6	6.3 ± 0.4	5.8

^{a} Determined for the data of Table IV, using eq 5. ^{b} Calculated from the Eyring equation with $\Delta H^{\ddagger} = 6.63 \pm 0.95$ kcal mol^{-1} and $\Delta S^{\ddagger} = -41 \pm 3$ cal deg^{-1} mol^{-1} with rms = 3.18%. ^{c} As for b but with $\Delta H^{\ddagger} = 15.1 \pm 1.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -19 \pm 5$ cal deg^{-1} mol^{-1} with rms = 6.13%.

studied under pseudo-first-order conditions (Cr(III) in excess), confirmed the numerical value of the reported rate constants, but analysis of the acid dependence of the observed rate constant at various temperatures (Table IV) showed that a much better fit of the experimental data was obtained using eq 5, rather than eq 6 which was used by the previous investigators.[4] This difference is probably attributable to the

$$k_{obsd} = k_s' + k_s''[H^+]^{-2} \tag{5}$$

$$k_{obsd} = k_6'[H^+]^{-1} + k_6''[H^+]^{-2} \tag{6}$$

higher ionic strength and, perhaps more importantly, to the greater range of acid concentration (0.05–0.25 M) used in the present study. The above acid dependence presumably indicates the participation of reactions 7 and 8 in the mechanism.
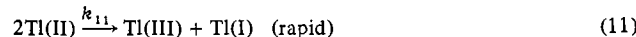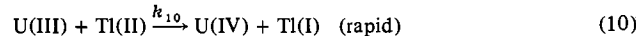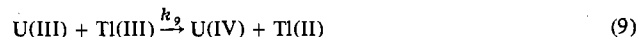
$$U^{3+} + Cr^{3+} \xrightarrow{k_7} [U\cdot Cr]^{6+} \tag{7}$$

$$U^{3+} + Cr(OH)_2 \xrightarrow{k_8} [U\cdot Cr(OH)_2]^{4+} \tag{8}$$
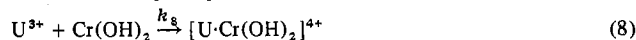
Although the participation of hydrolyzed U^{3+} species would provide an identical acid dependence, the hydrolysis constants of U^{3+} ions have been reported[11] to be of the order of 10^{-9} M^{-1} and would thus appear to be lower than the corresponding values for the Cr^{3+} ion, commonly quoted to be in the range 10^{-5}–10^{-6} M^{-1}.[12]
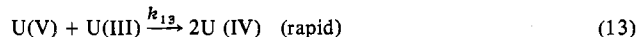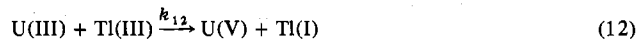
The temperature dependence of k_s' and k_s'' was analyzed in terms of the usual Eyring equation to yield the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ summarized in Table V.

Discussion

The second-order rate law and the stoichiometry described by eq 1 may be formally satisfied by two alternate reaction mechanisms involving either a one-electron transfer to form Tl(II) (eq 9) followed by either eq 10 or 11 or, alternatively,

$$U(III) + Tl(III) \xrightarrow{k_9} U(IV) + Tl(II) \tag{9}$$

$$U(III) + Tl(II) \xrightarrow{k_{10}} U(IV) + Tl(I) \quad \text{(rapid)} \tag{10}$$

$$2Tl(II) \xrightarrow{k_{11}} Tl(III) + Tl(I) \quad \text{(rapid)} \tag{11}$$

a two-electron transfer to yield U(V) (eq 12) to be followed

$$U(III) + Tl(III) \xrightarrow{k_{12}} U(V) + Tl(I) \tag{12}$$

$$U(V) + U(III) \xrightarrow{k_{13}} 2U(IV) \quad \text{(rapid)} \tag{13}$$

by the reaction of U(III) with U(V) (eq 13). Although neither of the above alternatives can be dismissed with complete certainty, the two-electron transfer (eq 12) appears unlikely since the oxidation reactions of uranium ions requiring the formation of the uranyl group are invariably slow[10] and usually show an inverse acid dependence which is much more pronounced than that observed in the present study. Typically, the oxidation of U(IV) by Tl(III) has a rate constant of 2.2 × 10^{-2} M^{-1} s^{-1} (20 °C, [H$^+$] = 1.0 M, I = 3.0 M^{-1}) and is dominated by a reaction path having an inverse second-order acid dependence. However, while eq 9 would appear to be the most likely rate-controlling step, both reactions 10 and 11 are equally probable choices for the subsequent reactions of the Tl(II) ions formed by eq 9. While reaction 11 has a reported[14] rate constant of 5 × 10^8 M^{-1} s^{-1} at 25 °C, the rate constant of reaction 10 is unknown but would seem unlikely to be as large as that of eq 11. It will be noted that if reaction 9 is followed by eq 10, the application of the steady-state approximation to the Tl(II) concentration readily shows that k_9 = $0.5k_4$ and that $\Delta S_9^{\ddagger} = (\Delta S_4^{\ddagger} - R \ln 2)$, but that if eq 9 is followed by eq 11, $k_9 = k_4$. Both alternatives however result in the stoichiometry represented by eq 1.

Examination of the rate constants for the various reaction paths for the reactions of U(III) ions studied to date (Table VI) suggests several notable features of which the consistent increase of k_0 to a limiting value of approximately 10^6 M^{-1} s^{-1} has already been the subject of a previous study.[2] Equally obvious is the dominance of the inverse acid concentration dependent reaction path for reactions of small $-\Delta G°$ values, the apparent absence of a contribution from this path to reactions of high $-\Delta G°$ values, and the striking similarity of the numerical value of k_{-1} first for the V(III), [Co^{III}-(NH$_3$)$_5$H$_2$O], and Tl(III) reactions and second to the limiting value of 10^6 M^{-1} s^{-1} observed[2] for k_0. It may be noted that Davies[18] has suggested a limiting rate of 3 × 10^6 M^{-1} s^{-1} for reactions involving the CoOH^{2+} ions, and other workers[19] have shown that the fastest reactions of the Cr^{2+} ion occur with rate constants in the range 10^6–10^7 M^{-1} s^{-1}. Moreover, examination of Table VII, which summarizes the rate constants for the OH-catalyzed reaction path of a wide variety of metal ions, shows that none has a value greater than 7 × 10^6 M^{-1} s^{-1} and that this limit is not confined to specific ions such as for example Cr(II) or Co(III). From the foregoing, it may be suggested that the above limiting rate is a feature of a wide variety of electron-transfer reactions and that it is equally applicable to reactions between hydrated metal ions and to reactions catalyzed by OH$^-$ ions.

The presence of a limit of approximately 10^6–10^7 M^{-1} s^{-1} for the rate constants of *both* the acid-independent and

Table VI. Comparison of the Rate Constants of Reaction Paths Observed for U(III) Reductions^a

Oxidant	$\Delta G°$, kcal mol^{-1}	k_0, M^{-1} s^{-1}	k_{-1}, M^{-1} s^{-1}	k_{-2}, M^{-1} s^{-1}	Ref
Cr(III)	−4.6	4.8 × 10^{-2}	n.o.^{d}	4 × 10–4 × 10^7	This work
V(III)	−8.6	5.4 × 10	1.4 × 10^5	n.o.	1
[Co(NH$_3$)$_5$H$_2$O]$^{3+}$ ^{b}	−9.1	2.8 × 10	2.7 × 10^5	n.o.	15
U(VI)^c	−15.2	5.5 × 10^4	n.o.	n.o.	16
Tl(III)	−21.6	n.o.	3.6 × 10^5	n.o.	This work
V(IV)	−22.3	3.7 × 10^5	n.o.	n.o.	1
Fe(III)	−31.8	3.9 × 10^5	n.o.	n.o.	1
Co(III)	−55.7	1.1 × 10^6	n.o.	n.o.	2

^{a} Rate constants k_0, k_{-1}, and k_{-2} refer to reaction paths $U^{3+} + M^{n+} \rightarrow [\ ]^*$, $U^{3+} + MOH^{(n-1)+} \rightarrow [\ ]^*$, and $U^{3+} + M(OH)_2^{(n-2)+} \rightarrow [\ ]^*$, respectively. Values are reported for a temperature of 20 °C and an ionic strength of 2.0 M. ^{b} At 25 °C, ionic strength 0.2 M. ^{c} At 25 °C, ionic strength 1.0 M. ^{d} Reaction path not observed.

Table VII. Comparison of the Rate Constants for Hydroxy Paths of Some Electron-Transfer Reactions

Reaction	$G°$, kcal mol^{-1}	k^{-1},^{a} M^{-1} s^{-1}	T, °C	μ	Ref
Cr(II)-Co(III)	-51.1	3.3×10^6	25	3.0	20
Eu(II)-Fe(III)	-27.7	7.0×10^6	25	1.0	21
Cr(II)-Fe(III)	-27.2	3.3×10^6	25	1.0	22
Yb(II)-Cr(III)	-26.5	1.6×10^5	25	0.2	23
Fe(II)-Co(III)	-23.9	6.5×10^3	0	1.0	24
U(III)-Tl(III)	-21.6	3.6×10^5	20	2.0	This work
V(IV)-Co(III)	-18.7	2.3×10^3	20	3.0	25
Fe(II)-Mn(III)	-17.0	7.4×10^5	20	3.0	26
Cr(II)-[Co(NH$_3$)$_5$H$_2$O]$^{2+}$	-16.3	1.5×10^6	25	1.0	27
Np(III)-Fe(III)	-14.4	3.0×10^5	25	2.0	28
Cr(II)-Cu(II)	-12.9	5.9×10^5	25	1.0	29
Cr(II)-Np(IV)	-12.6	8.4×10^2	25	1.0	30
U(IV)-Np(VI)	-12.2	5.2×10^2	25	2.0	31
U(III)-[Co(NH$_3$)$_5$H$_2$O]$^{3+}$	-9.1	2.7×10^5	25	0.2	3
U(III)-V(III)	-8.6	1.4×10^5	20	2.0	1
Fe(II)-Pu(IV)	-4.8	1.5×10^2	25	2.0	32
Eu(II)-V(III)	-4	2.0	25	1.0	33
Pu(III)-Pu(IV)	0	1.3×10^4	0	2.0	34
Co(II)-Co(III)	0	6.7×10^3	20	1.0	35
Fe(II)-Fe(III)	0	2.7×10^3	22	0.4	36
Cr(II)-Cr(III)	0	7	25	1.0	27
Tl(I)-Tl(III)	0	3.2×10^{-2}	25	3.7	38

^{a} Rate constants k^{-1} refer to reaction paths of the type A^{n+} + BOH$^{m+} \rightarrow$ [ ]*. Values of k^{-1} that were not specifically given in the literature were calculated from the empirical acid relationship using an appropriate hydrolysis constant obtained from ref 12.

OH-catalyzed reaction paths would provide a very simple explanation for the apparent absence of an inverse acid dependent reaction path for the reactions of V(IV), Fe(III), and Co(III) with U(III). Thus if for all three reactions the values of k_{-1} are in the range 10^6–10^7 M^{-1} s^{-1}, while the hydrolysis constants of the ions involved are in the range 10^{-3}–10^{-4} M^{-1}, it follows that the $\{K_H k_{-1}/[H^+]\}$ term of eq 14 will make a

$$k_{obsd} = k_0 + \{K_H k_1/[H^+]\} \tag{14}$$

statistically insignificant contribution to k_{obsd} over the acid concentration range 0.10–2.0 M usually employed and that the reactions will consequently appear to be acid independent. Only for reactions in which k_0 falls substantially below the limiting value, as for example in the Co(III)–Cr(II) reaction ($k_0 = 1.25 \times 10^4$ M^{-1} s^{-1}),[20] will the OH-catalyzed path begin to reveal itself.

The origin of the limiting rates for both the acid-independent and OH-catalyzed reaction paths for electron-transfer reactions between hydrated metal ions is not obvious. Control by the rate of substitution of one reactant into the inner coordination sphere of the other seems an unlikely explanation since ions such as Cr(II), Eu(II), Yb(II), and U(III) are all characterized by very high (10^8–10^9 M^{-1} s^{-1}) water-exchange rates, although ^{18}O transfer has been demonstrated for the Cr^{II}–Co^{III}-(NH$_3$)$_2$H$_2$O reaction.[27] The limiting rate of CoOH^{2+} has been attributed[18] to the participation of a precursor complex and, alternatively, to the thermal spin crossover of Co(III) ions,[39] while the same effect observed for the reactions of Cr(II) has been assigned to the distortion required at the Cr(II) center

to satisfy the Frank–Condon principle.[19b] These explanations are clearly not of general applicability, and it would seem that the correct explanation should provide a common reaction mechanism for a variety of different reactions and would probably involve the only common feature in these reactions, viz., the water molecules constituting the inner and outer coordination spheres of the ions and the solvent in which these reactions are studied.

References and Notes

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