Rates of Reduction of Some Cobalt(III) and Chromium(III) Complexes by Ytterbium(II)†

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Summary Kinetic studies on some reactions of the very strongly reducing bivalent lanthanide ion Yb^{2+} have been performed, with results indicating mechanisms comparable to Eu^{2+} reactions, although the Yb^{2+} rates are much higher.

AQUEOUS solutions of Yb^{2+} can liberate hydrogen from water because $E°$ is $-1{\cdot}15$ v.[1] Nevertheless, quantitative kinetic studies on some of its fast reactions can be realized, because Yb^{2+} solutions generated electrochemically in 10^{-3}—10^{-1} M-perchloric acid decompose slowly. We have performed kinetic measurements on the reduction of several Co^{III} and Cr^{III} complexes by Yb^{2+}, representing the first kinetic studies reported on Yb^{2+} reactions. Adamson[2] considered a study of the Yb^{2+}—Yb^{3+} electron exchange rate, but did not attempt it after finding Yb^{2+} solutions were not sufficiently stable.

The complexes $Co(NH_3)_6{}^{3+}$ and $Co(en)_3{}^{3+}$ necessarily react with Yb^{2+} by outer-sphere (os) mechanisms:

$$CoL_6{}^{3+} + Yb^{2+} \rightarrow Co^{2+} + Yb^{3+} + 6L \qquad (1)$$

Both reactions follow second-order kinetics (Table 1) and occur much more rapidly than the corresponding reactions of other reducing agents. In the case of $Co(NH_3)_6{}^{3+}$, for example, the values of k_2, $M^{-1}s^{-1}$, are $2{\cdot}28 \times 10^3$ (Yb^{2+}), 1·2 (U^{3+})[3], $1{\cdot}7 \times 10^{-3}$ (Eu^{2+})[4], and $8{\cdot}8 \times 10^{-5}$ (Cr^{2+}).[5] The reactions are strongly catalysed by anions; the effect of free chloride ion on the apparent rate constant is illustrated in

TABLE 1. *Rate constants for* Yb^{2+}–Co^{III} *reactions*[a]

Complex	$10^4[Co^{III}]_0$, M[b]	$[H^+]$, M	$10^{-3}k_2$, $M^{-1}s^{-1}$	$10^{-3}k_{Cl}$, $M^{-2}s^{-1}$
$Co(NH_3)_6{}^{3+}$	5·5—40·1	0·006—0·056	2·28	19·4
$Co(en)_3{}^{3+}$	21·2—150	0·005—0·051	0·45	4·73
$Co(NH_3)_5H_2O^{3+}$	3·0–10·8	0·005—0·20	31·5	158

[a] 25·0° and 0·20 *M* ionic strength.

[b] Most of the runs were carried out under pseudo-first-order conditions, with $[Yb^{2+}]_0 \leqslant 10\,[Co^{III}]$. A typical initial Yb^{2+} concentration was 2×10^{-4} M.

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the Figure. The kinetic data are consistent with the rate law

$$-\mathrm{d}[Yb^{2+}]/\mathrm{d}t = (k_2 + k_{Cl}[Cl^-])[Yb^{2+}][CoL_6^{3+}] \quad (2)$$

Values of k_{Cl} for the Yb^{2+} reactions are also given in Table 1. Again taking $Co(NH_3)_6^{3+}$ as an example, values of k_{Cl}/k_2, M^{-1}, are 8·5 (Yb^{2+}), 20 (U^{3+}),[3] and 140 (Cr^{2+}).[5] (The corresponding catalysis has not been reported for Eu^{2+}.) We suggest that the strong anion catalysis of OS reactions results from the role of X^- as a pseudo-bridging ligand, the mechanism being the reduction of $CoL_6^{3+}\cdot X^-$ by M^{2+}.[6] The rates of reduction of $Co(NH_3)_5H_2O^{3+}$ by Yb^{2+} and Eu^{2+} are independent of $[H^+]$, but the latter reaction occurs more slowly ($k_2 = 0\cdot074\ M^{-1}s^{-1}$).[4] In contrast, the Cr^{2+} reaction rate[7] varies as $1/[H^+]$, implicating the inner-sphere (IS) reduction of $Co(NH_3)_5OH^{2+}$. The OS mechanism suggested for Eu^{2+}[4] appears applicable also to Yb^{2+}; this suggestion finds support in the pronounced catalytic effect of chloride ions: $k_{Cl}/k_{H_2O} = 5\cdot0$ (Yb^{2+}). In contrast, the IS reactions of Cr^{2+} with this oxidizing agent and others[8] are subject to only a very small acceleration by free anions.

We have also studied the kinetics of a series of reactions of $Cr(NH_3)_5X^{2+}$ complexes, having determined that most members of the series $Co(NH_3)_5X^{2+}$ are reduced at rates too high to measure. The Cr^{III} complexes react as shown in the equation,

$$Cr(NH_3)_5X^{2+} + Yb^{2+} + 5H^+ \rightarrow Cr^{2+} + Yb^{3+} + X^- + 5NH_4^+ \quad (3)$$

and follow a simple second-order rate expression. The rate constants for the halide complexes (Table 2) exhibit the relative order F > Br > Cl, which is unusual because other reducing agents show a smooth trend, in one direction or the other, with halide variation.[3,9] The minimum at X = Cl^- appears to represent only the particular balance struck in the relative ability of different halide ions to stabilize $Cr(NH_3)_5^{3+}$, in comparison to the binuclear intermediate $(NH_3)_5CrXYb^{4+}$ which precedes electron transfer in the IS mechanism.[10] Support for the IS mechanism also comes from the very feeble effect of anions; *e.g.*, 0·09 M free Cl^- increases the rate constant for $Cr(NH_3)_5Cl^{2+}$ by 11% (k_{Cl}/k_2 *ca.* 1·2 M^{-1}), for $Cr(NH_3)_5F^{2+}$ by 16% (k_{Cl}/k_2 *ca.* 1·8 M^{-1}), and for $Cr(NH_3)_5Br^{2+}$ by 7% (k_{Cl}/k_2 *ca.* 0·8).

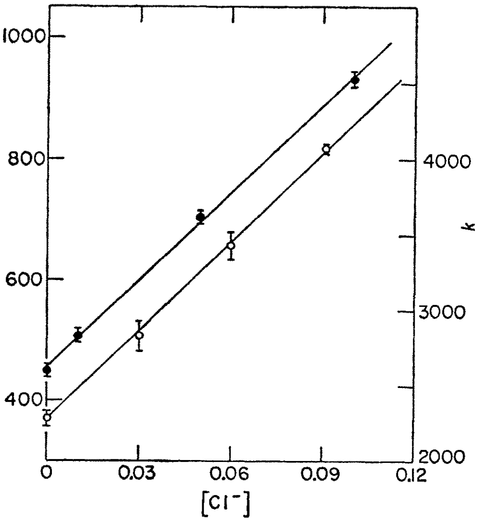

FIGURE. *Chloride dependence of the apparent second-order rate constants for* Co^{III}–Yb^{II} *reactions. Upper line (left ordinate scale),* $Co(en)_3^{3+}$; *lower line (right ordinate scale),* $Co(NH_3)_6^{3+}$.

TABLE 2. *Rate constants for* Yb^{2+}–$Cr(NH_3)_5X^{2+}$ *reactions*[a]

Complex	10^4x$[Cr^{III}]_0$,M[b]	$[H^+]$,M	k_2,$M^{-1}s^{-1}$
$Cr(NH_3)_5F^{2+}$	2·8—201	0·01—0·10	40·2
$Cr(NH_3)_5Cl^{2+}$	7·3—197	0·008—0·017	9·50
$Cr(NH_3)_5Br^{2+}$	6·6—36·2	0·008—0·100	14·2

[a] 15·8° and 0·20 *M*-ionic strength.

[b] The range of $[Yb^{2+}]_0$ was varied from *ca.* 1 to 6 × 10^{-4} M; pseudo first-order conditions were applicable to about half the runs.

A similar reactivity order F > Br > Cl was found for the reductions of $Cr(H_2O)_5X^{2+}$ complexes by Yb^{2+}, where the results[11] also lend strong support to the IS mechanism suggested for the $Cr(NH_3)_5X^{2+}$, by virtue of the much higher reactivity of CrN_3^{2+} than $CrNCS^{2+}$.[12]

Although a considerable number of studies have been carried out on Eu^{2+} reductions, the deduction of the detailed mechanisms have often been made by comparisons to first-row transition-metal reducing agents, *e.g.* Cr^{2+}, V^{2+}, and Fe^{2+}. The present findings for Yb^{2+} help to validate the mechanisms suggested and many of the comparisons attempted earlier.

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