Kinetic Studies on the Redox Reactions of Uranium(III)†

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Summary Studies on the rates of reduction of cobalt(III) and chromium(III) complexes by uranium(III) in perchloric acid solution have been carried out, with results indicating an inner-sphere mechanism in which hydroxide is a particularly favourable bridging ligand.

URANIUM(III) is one of the most powerful homogeneous reducing agents in aqueous solution, with a reduction potential for the U^{4+}/U^{3+} couple of $-0{\cdot}63$ v in perchloric acid solution.[1] The kinetics of the oxidation–reduction reactions of U^{3+} have not been studied previously; the occurrence of such reactions has gone largely unnoted. We have undertaken a kinetic study on a number of such reactions, particularly those which, for other reducing agents, have proved most helpful in revealing the detailed mechanism.

TABLE. *Rate constants for* U^{III}–Co^{III} *reactions*[a]

Complex	$[Co^{III}]_0$, M	$[H^+]$, M	k, $M^{-1}sec^{-1}$
$(NH_3)_5CoN_3^{2+}$	8×10^{-5}	0·05	8×10^5
$(NH_3)_5CoF^{2+}$	8×10^{-5}	0·05	$3{\cdot}8 \times 10^5$
$(NH_3)_5CoCl^{2+}$	$(4\text{—}6) \times 10^{-4}$	0·05	$3{\cdot}2 \times 10^4$
$(NH_3)_5CoOAc^{2+}$	$(4\text{—}12) \times 10^{-4}$	0·01—0·19	$1{\cdot}5 \times 10^4$
$(NH_3)_5CoBr^{2+}$	$(3\text{—}19) \times 10^{-4}$	0·01—0·19	$1{\cdot}4 \times 10^4$
$(NH_3)_5CoCN^{2+}$	$(6\text{—}11) \times 10^{-4}$	0·05	$3{\cdot}5 \times 10^3$
$(NH_3)_5CoNCS^{2+}$	$(4\text{—}11) \times 10^{-4}$	0·02—0·05	18[b]
$Co(NH_3)_6^{3+}$	1×10^{-3}	0·05	1·2[c]
$Co(en)_3^{3+}$	5×10^{-3}	0·05	0·13[c]

[a] Second-order rate constants at 25·0° and 0·20 M-ionic strength.

[b] Confirmed with two independent, nitrate-free samples (see ref. 12).

[c] In chloride-free solutions; there is an additional term exhibiting a linear dependence upon the concentration of free chloride ion.

The U^{III} solutions were prepared shortly before each experiment by reduction of U^{4+} or UO_2^{2+} solutions, as perchlorates, using amalgamated zinc or electrolytic reduction at a mercury pool cathode. In this way, possible difficulties arising from storage of the unstable U^{III} solutions are avoided, although both reduction of the solvent and of perchlorate ion by 10^{-3} M-U^{III} were found to be negligible, as had been reported by Sato.[2] The reaction rates of interest here were evaluated spectrophotometrically using the stopped-flow technique for the faster members.[3,4]

Cobalt(III) complexes are readily reduced to Co^{2+} by U^{3+}; oxidation of U^{III} stops at U^{4+}, as indicated by the example of $(NH_3)_5CoX^{2+}$ in reaction (1). For all complexes studied, the 1 : 1 stoicheiometry

$$(NH_3)_5CoX^{2+} + U^{3+} + 5H^+ = Co^{2+} + U^{4+} + 5NH_4^+ + X^- \qquad (1)$$

has been verified‡ and the products Co^{2+} and U^{4+} identified. In most experiments, U^{3+} was present at much lower concentration than the Co^{III} complex. The rate constants were evaluated by standard methods.[5] The second-order rate expression was confirmed by the constancy of k over a considerable range of concentrations (see Table).

Two features are particularly worthy of note: the "inverted order" of halide reactivity,[6-8] and the high rate ratio of the azido- compared to the isothiocyanato-complex.[9,10]§ The inverted order was also found for the same reductions accomplished by Fe^{2+} [9,11] and Eu^{2+},[6] in contrast to Cr^{2+},[12] V^{2+},[7,11] and Cu^+.[5] The reactivity order is, in itself, not diagnostic of mechanism and one must consider the stabilities of the different X-containing transition states (relative to one another).[8] Following the method of Haim,[8] in the present case the transition state containing F^- is the most stable, and that containing Br^- the least. This corresponds to the pattern found for all the inner-sphere mechanisms,[5,7,8] although it is not a sufficient criterion of mechanism because the outer-sphere reactivity pattern is not necessarily different (in the two known cases the pattern Br > Cl > F was noted, however). The substantially higher reactivity of the azido-complexes ($k = 8 \times 10^5$) compared to the isothiocyanato-complex ($k = 18$) provides supporting evidence for the inner-sphere mechanism.[9,10] The low rate of reaction of $Co(NH_3)_6^{3+}$ is expected regardless of whether the other complexes react by inner- or outer-sphere mechanisms; Patel and Endicott concluded that even outer-sphere reactions may show considerable ligand selectivity owing to the necessity of stretching critical bonds in the oxidizing complex.[13] Irrespective of whether an anion is bridging or not, a five-co-ordinate Co^{II} intermediate may be the immediate decomposition product of the "successor complex."[14]

The reduction of Cr^{III} complexes to Cr^{2+} is readily accomplished by the strongly reducing U^{3+} solutions. Reduction of members of the series $(H_2O)_5CrX^{2+}$ is shown in reaction (2), and occurs according to

$$CrX^{2+} + U^{3+} = Cr^{2+} + X^- + U^{4+} \qquad (2)$$

the rate expression

$$-d[U^{3+}]/dt = (a + b/[H^+])[CrX^{2+}][U^{3+}]. \qquad (3)$$

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† Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

‡ In a number of complexes other than those considered here *e.g.*, X = NO_3^-, NO_2^-, and ONO^-, substantial ligand reduction occurred.

§ Early experiments with $[Co(NH_3)_5NCS](ClO_4)_2$ gave substantially higher rate constants, of the order of 10^5 M^{-1} sec^{-1}, but the two independent samples of the complex used for that work contained traces of nitrate ion, which reacts rapidly with U^{3+}. The very carefully purified complex reacted more slowly, and gave reproducible rate behaviour and an exact 1 : 1 stoicheiometry.

The dependence of the apparent second-order rate constant upon $[H^+]$ given in equation (3) is illustrated in the Figure. It is seen that for the Cl^- and Br^- complexes *a* is negligibly small, whereas for CrF^{2+} *a* has the value 17 M^{-1} sec^{-1}. (This behaviour parallels that for the same complexes upon reduction by Cr^{2+} in the path which is not halide-bridged.[15]) The values of the rate parameter *b* are CrF^{2+} — 0·31, $CrCl^{2+}$ — 0·50, and $CrBr^{2+}$ — 1·4 sec^{-1} at 25·0° and μ = 0·20 M. The inference drawn from equation (3) is that the conjugate base complex, $(H_2O)_4Cr(OH)X^+$, has a high reactivity. The hydroxo-bridged transition state may be favoured over the halide because the U^{4+} ion is quite acidic.[16] In support of this, very slow reduction of $(NH_3)_5CrCl^{2+}$ (*k ca.* 0·008) was noted.

Further work on similar systems is in progress, including extension of these studies to aquo- and aquo-halo-complexes of Co^{III}. Other oxidants are being studied: VO^{2+}, Cr^{3+}, V^{3+}, Cu^{2+}, UO_2^{2+}, and Fe^{3+} are all reduced by U^{3+} at measurable rates.

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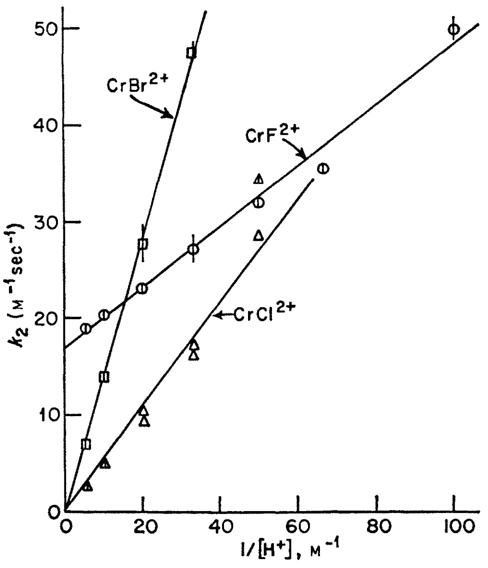

FIGURE. *The apparent second-order rate constants for* CrX^{2+} *complexes plotted* versus $1/[H^+]$, *as indicated by equation* (3).

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