Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam
Printed in the Netherlands.

ELECTRON TRANSFER REACTIONS INVOLVING TITANIUM(III)*

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Electron transfer reactions may be classified as either inner-sphere or outer-sphere. In the former, one of the original ligands forms a bridge between the two reacting centers; in the latter, there is no interpenetration of the coordination shells. The reactions are of some importance, since they provide a tool for structure investigation and for the preparation of new complexes[1,2,3]. The theory of outer-sphere electron transfers has been studied in more detail than that of inner-sphere reactions, and this is due partly to the difficulty in preparing model complexes whose reductions will give meaningful results.

In general, the variations in rate constants observed for the reduction of a series of complexes with a particular reductant are quite small (Table I), while the rate constants for the reduction of a particular complex with a series of reductants show large differences (Table II). In an attempt to introduce larger changes in rates of reduction, a series of complexes containing oxyanions as the electron transfer mediator has been prepared and treated with chromium(II), vanadium(II), and

TABLE I

SPECIFIC RATES FOR THE Cr^{II} REDUCTION OF HALOPENTAMMINECOBALT(III) IONS[4] AT 25 °C

Complex	*k*($M^{-1}sec^{-1}$)
fluoro	$2.5 \cdot 10^5$
chloro	$6 \cdot 10^5$
bromo	$1.4 \cdot 10^5$
iodo	$3 \cdot 10^5$

TABLE II

SPECIFIC RATES FOR THE REDUCTION OF CHLOROPENTAMMINECOBALT(III) ION AT 25°; $\mu = 1.0$

Reductant	*k*($M^{-1}sec^{-1}$)
Cr^{II} (ref. 4)	$6 \cdot 10^5$
V^{II}	6.4
Eu^{II} (ref. 4)	$3.9 \cdot 10^2$
Ti^{III}	$1.8 \cdot 10$

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* This research was supported by a grant from the National Science Foundation.

** Alfred P. Sloan Foundation Fellow, 1964–1966.

europium(II)[5]. This paper reports the results of some electron transfer experiments using titanium(III), both as the sulfate and the perchlorate, as reductant.

Titanium(III) will form a 1:1 complex with titanium(IV) in sulfate solution. The complex possesses a broad absorption band in the region 4000 Å to 7000 Å, with $\varepsilon = 30$ at 5150 Å, the wavelength of maximum absorption. The stability constant is approximately 110 at 25 °C. Rates of reaction were determined by following the rate of disappearance of the Co^{III} absorption at 3500 or 5000 Å. The overall reaction is

$$Ti^{III} + (NH_3)_5CoX^{n+} + 5H^+ \rightarrow Ti^{IV} + Co^{II} + 5NH_4{}^+ + X$$

and all the reductions studied were second order processes, first order in both complex and reductant. Kinetic measurements were made either with an excess of reductant (pseudo first order) or with equal initial concentrations of the two reactants. The concentration of the cobalt(III) species at any time was obtained from the expression

$$[Co^{III}] = \frac{A_t - b\varepsilon_p[Co^{III}]_0}{b(\varepsilon_R - \varepsilon_p)}$$

where A = absorbance of solution at time t, b = cell path length, and ε_R and ε_p = extinction coefficients of the reactants and products respectively.

All of the rate plots (obtained by plotting log $[Co^{III}]_t$ *vs.* time or $[Co^{III}]_0/[Co^{III}]_t$ *vs.* time) were curved, as shown in Fig. 1. The rate law best describing the observed behavior in the pseudo first order reactions is

$$-d[Co^{III}]/dt = k \cdot a([Co^{III}]_t - [Ti^{IV}]_t) + k' \cdot a[Ti^{IV}]_t \qquad (1)$$

Experiments showed that neither Co^{II} nor the free ligand X liberated during the reaction were responsible for the inhibition. Addition of Ti^{IV}, on the other hand, caused a marked decrease in the rate of reaction. The mechanism suggested is therefore

$$\begin{aligned}
&(NH_3)_5Co^{III}X + Ti^{III} \rightarrow Co^{II} + X + Ti^{IV} && k\\
&(NH_3)_5Co^{III}X + Ti^{IV} \rightarrow (NH_3)_5Co^{III}X \cdot Ti^{IV} &&\\
&(NH_3)_5Co^{II}X \cdot Ti^{IV} + Ti^{III} \rightarrow Co^{II} + X + 2Ti^{IV} + 5NH_4{}^+ && k'
\end{aligned}$$

Table III lists some values of the specific rates k and k'.

There is always some uncertainty as to the detailed mechanism of an electrons transfer if the oxidized form of the reactant is substitution-labile. It has been suggested[4] that a comparison of a series of specific rates with those obtained from the vanadium(II) reduction of the same complexes can be used as a guide; for example, the rate constants for the europium(II) reduction of the halopentamminecobalt(III) complexes decrease as those for vanadium(II) increase, and this has been interpreted as an indication of an inner-sphere mechanism for Eu^{II} reductions. Table IV lists some specific rates determined for Ti^{III} and V^{II} reductions

TABLE III

SPECIFIC RATES FOR REDUCTIONS BY TITANIUM(III) SULFATE AT 25 °C; $\mu = 0.52$

Complex	*k($M^{-1}sec^{-1}$)*	*k'($M^{-1}sec^{-1}$)*
(a) pentaammines		
fluoro	110 (2°)	–
chloro	1.11	0.23
bromo	1.51	0.42
iodo	0.90	0.29
aquo	0.022	0.06
sulfato	0.32	0.038
(b) tetraammines		
diaquo	6.87	0.19
aquosulfato	6.33	1.45
sulfato (bridged)	7.60	1.65
sulfato (chelated)	2.37	1.72

TABLE IV

SPECIFIC RATES AT 25.0 °C ($M^{-1}sec^{-1}$)

Complex	*$Ti_2(SO_4)_3$*	*VSO_4 $\mu = 0.25$*	*$V(ClO_4)_2$ $\mu = 1.0$*
Fluoro	—	10.7	2.6
Chloro	1.11	14.5	5
Bromo	1.51	77	25
Iodo	0.90	—	120
Aquo	0.022	18.3	0.5
Sulfato	0.32	16.7	7.8

TABLE V

SPECIFIC RATES

Complex	*Ti^{III} 2 °C*	*Ti^{III} 25 °C*	*Eu^{II} 25 °C*
Fluoro	110	—	$2.6 \cdot 10^4$
Chloro	3.6	3.8	$3.9 \cdot 10^2$
Bromo	0.41	1.2	$2.5 \cdot 10^2$
Iodo	0.52	1.6	$1.2 \cdot 10^3$
Aquo	0.0018	0.022	0.15
Sulfato	0.028	0.15	$1.4 \cdot 10^2$

in sulfate solution, and for V^{II} reductions in perchlorate. Table V compares some specific rates for Ti^{III} and Eu^{II} reactions. It is clear that the behavior of Ti^{III} is much more like that of Eu^{II} than of V^{II}, so that reductions by titanium may be regarded as proceeding via an inner-sphere mechanism. Although the same trends are observed for V^{II} reductions in both sulfate and perchlorate media, it seemed worthwhile attempting to prepare solutions of titanium(III) perchlorate, in spite of their known instability, and using them for oxidation–reduction experiments. The most convenient method is electrolytic reduction of titanium(IV) sulfate in sulfuric acid. Immediately before the kinetic measurements, a sample of the titanium(III) is run into barium perchlorate ($[ClO_4^-] = 2[SO_4^{2-}]$), the mixture centrifuged in an atmosphere of nitrogen, and the resulting solution drawn up into a syringe fitted with a filter membrane (pore size 0.45 μ). At an ionic strength of one, the rate of perchlorate reduction is less than $3 \cdot 10^{-5} M^{-1}\text{sec}^{-1}$ at 25 °C. Good reproducibility can be obtained. Titanium(III) does not form the 1:1 complex with titanium(IV) in perchlorate solutions, nor do the rate plots show any curvature. Table VI lists some of the rate constants obtained for redox reactions of titanium(III) perchlorate.

TABLE VI

SPECIFIC RATES FOR TITANIUM(III) PERCHLORATE REDUCTIONS AT 25 °C; $\mu = 1.0$

Complex	*k* ($M^{-1}sec^{-1}$)
fluoro	36.5
chloro	17.5
bromo	24.5
iodo	25.1

DISCUSSION

Because it was not possible to measure the rates of titanium(III) sulfate reductions in solutions with an ionic strength higher than 0.52, a series of measurements were made with vanadium(II) in solutions of both 0.52 and 1.0 (Table IV). These measurements showed in fact that the trends at the higher ionic strength were preserved at the lower: there was no reversal, and so meaningful comparisons can be made between titanium sulfate and vanadium perchlorate reductions. The curvature observed in the titanium sulfate rate plots is not due to the formation of the 1:1 titanium(III)–(IV) intermediate—especially in the case of the pseudo first order measurements, the decrease in free $[Ti^{III}]$ is very small, whereas the change observed in the rate is large (Table III; the change in the case of the chloro complex, for example, is a factor of 4.8).

The integrated form of the rate law is

$$\ln a - \ln(a - [2k - k']/k \cdot x) = (2k - k')bt, \tag{2}$$

where b is the concentration of the titanium(III). This has two limiting forms; one when $k = k'$ (no inhibition), giving a straight line plot with a slope of kb. The second limiting form occurs when $k' = 0$ (complete inhibition) and gives a straight line with slope of $2kb$. Fig. 1 shows these two limiting cases, together with the line obtained by substitution in equation (2) for the chloropentammine using the experimentally determined values of $k_{\text{init.}}$ ($= kb$) and $k_{\text{final}} = (k'b)$. The slope obtained is 0.065, in very good agreement with that calculated (0.068).

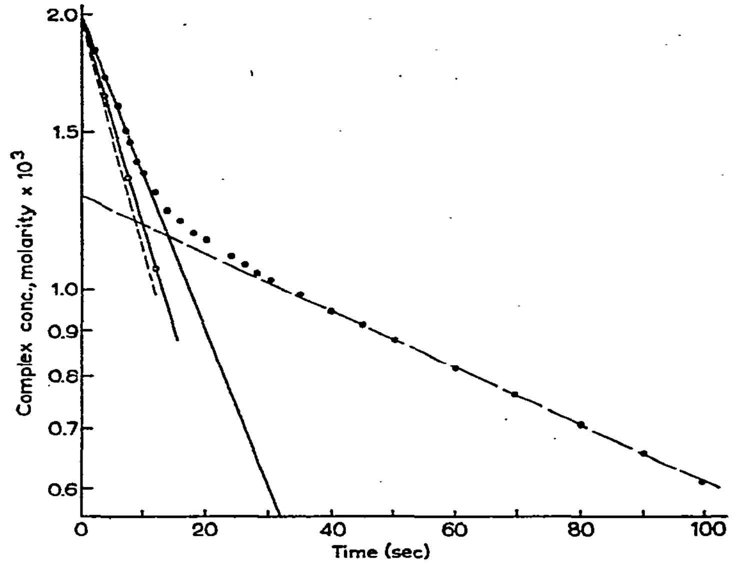

Fig. 1. Rate plot of $Ti^{III}+Co(NH_3)_5X^{3+}$

——— *k* ——O—— observed

— — — *k'* ------ *k'* = 0

All the rate plots obtained for reactions of titanium(III) perchlorate are linear, with no inhibition, and the trends obtained (for example, Table VI) parallel those for the *k* values of the sulfate.

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