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# Reduction of Co(III) Oxidants by Ti(III)

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Cope, Miller and Fraser[1] reported that $Ti^{3+}$ reacts with $Co(NH_3)_5Cl^{2+}$ in a fairly rapid acid-independent reaction in $Cl^-$ and $SO_4^{2-}$ media containing substantial amounts of $ClO_4^-$. They also reported complicated anion effects. Duke and Quinney[2] had previously studied the reaction of $Ti^{3+}$ with $ClO_4^-$ and kinetically determined that the stability constant of the $TiCl^{2+}$ complex was 2.2 at 40 °C. Rosseinsky[3] considered data in the literature on reactions of simple reductants $M^{2+}$ with various $Co(III)A_4XY$ species. He correlated the differences in selectivity (with respect to variations in Y) in terms of a semi-theoretical model which leads to the expectation that redox potential of $M^{2+}$ determines the selectivity of $M^{2+}$ for reaction with various Co(III) species. We now report studies of reaction of $Ti^{3+}$ in various aqueous media which call into question, to a more or less severe degree, all of the reports mentioned above.

Solutions in $Cl^-$, $CF_3SO_3^-$ and *para*toluenesulfonate (hereafter tosylate or $Tos^-$) media, $[Co(NH_3)_5Cl]Cl_2$ and *cis* and *trans*-$[Co(en)_2Cl_2]Cl$ were all prepared by standard methods, and the reaction of Co(III) oxidants with Ti(III) was studied spectrophotometrically at 25.2 °C. In the tosylate media used, zero-order kinetics were observed and results were erratic. Various methods of recrystallization of HTos did not change these results. In $CF_3SO_3^-$ media of constant acidity, the Co(III)–$Ti^{3+}$ reaction proceeded with 1/1 stoichiometry and reproducibly followed the rate law,

$$v = k[Ti^{3+}][Co(III)].$$

The same kinetic behaviour (including the value of $k$) was observed in chloride media as in $CF_3SO_3^-$ media. We find no kinetic evidence of $TiCl^{2+}$.

The acid dependence of $k$ was adequately fitted by

$$k = \frac{k_0 + kK[H^+]^{-1}}{1 + K[H^+]^{-1}}$$

where the values of parameters are given in Table I.

TABLE I. Kinetic Parameters for Co(III)–$Ti^{3+}$ Reactions at 25.2 °C and Ionic Strength 1 *M* in $Cl^-$ or $CF_3SO_3^-$ Media.

| Oxidant | $k_0 \times 10^3$, $M^{-1}$ sec$^{-1}$ | K × $10^3$, $M^{-1}$ | $k$ $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| $Co(NH_3)_5Cl^{2+}$ | <.1 | 4.6[a] | .48 |
| *cis*-$Co(NH_3)_5Cl_2^+$ | 2 | 4.6[b] | .75 |
| *trans*-$Co(NH_3)_5Cl_2^+$ | 9 | 4.6[c] | 2.8 |

[a] Determined by standard methods from 26 kinetic runs. [b] Assumed, fitted 11 kinetic runs within ± 5%. [c] Assumed, fitted 9 kinetic runs within ± 6%.

The value of K measured kinetically is consistent with the hydrolysis constant of $Ti^{3+}$ measured[4] potentiometrically in $Br^-$ media ($K_h = 6.9 \times 10^{-3}$). We therefore infer that $TiOH^{2+}$ is the reductant in all three reactions. The values of $k$ that we report are several orders of magnitude less than that reported by Fraser, *et al.* We find more rapid rates and chloride-inhibition in perchlorate media. We conclude that in such media paths involving $ClO_4^-$ are dominant but may be quenched by $Cl^-$.

The Ti(IV) product would be expected to be $TiO^{2+}$ or a related polymer (*cf.* $VO^{2+}$). The efficiency of $TiOH^{2+}$ may be related to a reduced barrier due to less difference in structure between the Ti(III) and Ti(IV) forms involved. Since $TiOH^{2+}$ is intermediate in reducing power between $V^{2+}$ and $Ru^{2+}$, one would expect[3] that the difference between the *cis* and *trans* oxidants would be more than that observed for $V^{2+}$ but less than observed for $Ru^{2+}$. The observation of a smaller difference suggests that additional factors (*e.g.*, Ti(III)–Co(III) interaction prior to the transition state) are involved.

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