

Autocatalysis in a Ru(III)–Ti(III) Redox Reaction

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Previously, autocatalysis was observed in the reduction of $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$ by Ti(III) in CF_3SO_3^- media [1]. Addition of chloride removed the autocatalytic path, indicating that a relatively simple mechanism is involved [2]. We now report autocatalysis in the same reaction in chloride media. We have traced the origin of this autocatalysis to trace impurities of Cr(III), but the mechanism (probably heterogeneous) of this catalysis remains obscure.

Experimental details were generally as previously described [1], except that both stainless steel and platinum needles were employed. All reactions were carried out in 0.9 M LiCl/0.1 M HCl at 25 °C, with Ti(III) in at least ten-fold excess. Various preparations of Ti(III) gave similar results. In the absence of autocatalysis, pseudofirstorder rate plots were linear for three half-times and gave rate constants agreeing with those reported earlier [1]. For reac-

tions showing autocatalysis, pseudofirstorder rate plots were not linear. The reaction was at least 75% completed at the time corresponding to the half-time calculated from the initial slope.

Autocatalysis was absent when platinum needles were used and when Fe(II), Fe(III), Mn(II), Ni(II), Co(II) or Cu(II) salts were added in low (0.1 mM) concentration, but was present when stainless steel needles were used, or when traces of chromium(III) salts were added. Autocatalysis persisted even with platinum needles if spectrophotometric cells were not thoroughly cleaned after a run in which Cr(III) was present. A sufficient rationalization for all these results is that chromium-containing surface films are responsible for the autocatalysis. On this basis, we expected that $\text{Cr}(\text{en})_3^{3+}$ would be catalytically inactive. We found, however, that even recrystallized $\text{Cr}(\text{en})_3\text{Cl}_3$, in 0.1 mM concentration, caused significant autocatalysis. The failure of this prediction may indicate that a more-complex mechanism is involved, or that even miniscule amounts of Cr(III) aquoions are sufficient to give the effect.

References

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