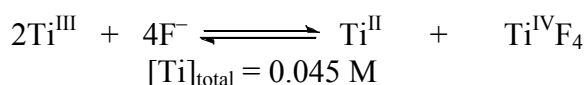


Table S-1. Spectrophotometric titration of Ti(III) by HF/F⁻ solution in 0.50 M CF₃SO₃H.



[HF], M	OD _{500nm} ^a	OD _{650nm} ^a	[Ti(III)], M ^b	10[Ti(II)], M
0.00000	0.185(0.184)	0.033(0.033)	0.045	0.0000
0.0045	0.182(0.183)	0.035(0.035)	0.044	0.005
0.0135	0.170 (0.172)	0.045(0.044)	0.038	0.033
0.0180	0.164 (0.164)	0.052(0.051)	0.034	0.054
0.0225	0.157 (0.157)	0.058(0.058)	0.030	0.074
0.0270	0.152(0.150)	0.064(0.064)	0.026	0.093
0.0314	0.145 (0.144)	0.070(0.070)	0.023	0.110
0.0359	0.139 (0.139)	0.075(0.075)	0.020	0.125
0.0404	0.134 (0.134)	0.079(0.079)	0.017	0.140
0.0449	0.130 (0.130)	0.082(0.084)	0.015	0.150
0.0493	0.126(0.127)	0.086(0.087)	0.013	0.158
0.0538	0.124(0.124)	0.090(0.090)	0.012	0.166
0.0583	0.120(0.121)	0.092(0.092)	0.010	0.173
0.0627	0.119 (0.119)	0.094(0.094)	0.009	0.178
0.0672	0.119(0.118)	0.096(0.095)	0.008	0.183

^aParenthetical OD values were calculated from eq (4) in conjunction with Appendix eq. (g), taking $K_{3,2}$ as $2.35 \times 10^5 \text{ M}^{-4}$ and extinction coefficients of Ti(III) (ϵ_3) and Ti(II) (ϵ_2) as follows:

$$\text{at } 500 \text{ nm } \epsilon_3 = 4.1 \text{ M}^{-1}\text{cm}^{-1}, \epsilon_2 = 4.5 \text{ M}^{-1}\text{cm}^{-1},$$

$$\text{at } 650 \text{ nm } \epsilon_3 = 0.74 \text{ M}^{-1}\text{cm}^{-1}, \epsilon_2 = 4.9 \text{ M}^{-1}\text{cm}^{-1}.$$

Satisfactory fittings were not obtained with $[\text{Ti}^{\text{IV}}\text{F}_3]^+$ or $[\text{Ti}^{\text{IV}}\text{F}_5]^-$.

^bConcentrations obtained from Appendix eqs. (g) and (e).

Table S-2. Variation of the disproportionation constant, $K_{3,2}$, with acidity.



$[\text{H}^+]$, M	$10^{-5} K_{3,2}$, M ⁻⁴
0.50	2.4 ± 0.2
0.35	3.1 ± 0.3
0.25	3.6 ± 0.2
0.100	4.0 ± 0.3

^a $[\text{Ti}]_{\text{total}} = 0.45$ M throughout; $\mu = 0.5$ M ($\text{CF}_3\text{SO}_3\text{H} + \text{CF}_3\text{SO}_3\text{Na}$). Values of $K_{3,2}$ were obtained by refinement of OD data.

Table S-3. Reductions of quinines using Ti(III) at high $[H^+]$ ^a

Quinone	λ , nm	$[Ti^{III}]$, mM	$[H^+]$, M	k_{obs} , s^{-1} ^b
1,4-Benzoquinone	246	1.00	0.50	0.151(0.152)
		2.0	0.50	0.30(0.30)
		4.0	0.50	0.61(0.60)
		8.0	0.50	1.22(1.21)
		1.00	0.35	0.175(0.172)
		1.00	0.25	0.200(0.197)
		1.00	0.10	0.33(0.33)
Chloranilic acid ^c	302	1.00	0.50	2.7(2.8)
		3.0	0.50	8.4(8.3)
		6.0	0.50	18.2(16.6)
		9.0	0.50	25(25)
		1.00	0.35	3.7(3.9)
		1.00	0.25	5.8(5.5)
		1.00	0.10	13.2(13.8)
Tetrahydroxy-1,4-benzoquinone	310	1.00	0.50	0.25(0.24)
		2.0	0.50	0.51(0.48)
		4.0	0.50	1.05(0.96)
		8.0	0.50	2.0(1.91)
		1.00	0.35	0.34(0.34)
		1.00	0.25	0.45(0.48)
		1.00	0.10	1.06(1.20)

Footnote of Table S-3

^areactions were run at 22.0 ± 0.5 °C. Acidity was maintained by triflic acid, $\mu = 0.5$ M (CF₃SO₃H/ CF₃SO₃Na), [quinone] = 0.05 mM.

^bPseudo-first order rate constants; parenthetical values were calculated using rate law 5.

^c2,5-Dichloro-3,6-dihydroxybenzoquinone