MECHANISM OF AUTOCATALYTIC Fe(phen)$_3^{2+}$ OXIDATION BY BROMATE

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Received January 16, 1979
Accepted March 12, 1979

Fe(phen)$_3^{2+}$ oxidation by bromate has been investigated at large excesses of bromate. The kinetics are consistent with the mechanism suggested earlier for the similar reaction of Ce$^{3+}$ oxidation.

RESULTS AND DISCUSSION

At $2.5 \times 10^{-4} \text{ M} \leq F \leq 2 \times 10^{-3} \text{ M}$, [Fe(phen)$_3^{2+}$] was measured spectrophotometrically at $\lambda = 635 \text{ nm}$. At $F = 2.5 \times 10^{-6} \text{ M}$, [Fe(phen)$_3^{2+}$] was measured at $\lambda = 505 \text{ nm}$. The error introduced by the other ferroin form was within 5%. The reaction was carried out at 15 $^\circ\text{C}$ under vigorous stirring.
The kinetic curves in Fig. 1 show the time dependence of [Fe(phen)$_3^{3+}$]. The reaction proceeds without deceleration until Fe(phen)$_3^{2+}$ is almost completely oxidized. Abrupt transitions to the steady state can be seen. At sufficiently small $F/h_0A$, the Fe(phen)$_3^{3+}$ concentration rises according to the law $[\text{Fe(phen)}_3^{3+}] \sim \exp(\alpha t)$. At sufficiently large $F/h_0A$, the exponential stage is replaced by the steady increase of [Fe(phen)$_3^{3+}$].

At $F = 2.5 \times 10^{-6}$ M for the set of concentrations: a) $A = 10^{-3}$, $[\text{H}_2\text{SO}_4] = 0.75$, b) $A = 10^{-3}$, $[\text{H}_2\text{SO}_4] = 1.5$, c) $A = 10^{-3}$, $[\text{H}_2\text{SO}_4] = 2$ and d) $A = 2 \times 10^{-3}$ M, $[\text{H}_2\text{SO}_4] = 1.5$ M, the following $\alpha$ increment values were obtained: a) 0.014, b) 0.045, c) 0.08, d) 0.1 s$^{-1}$, respectively. These data approximate well the expression $\alpha = q_1 h_0 A$.

At $F/h_0 A > 9.6 \times 10^{-5}$ M$^{-1}$ the rates, $V_s$, on the straight part of the kinetic curve were measured. At $A = 0.01$ M, $[\text{H}_2\text{SO}_4] = 1.5$ M the following $V_s$ values for various $F$ were obtained: a) $F = 2 \times 10^{-3}$, $V_s = 1.22$, b) $F = 10^{-3}$, $V_s = 1.29$, c) $F = 5 \times 10^{-4}$, $V_s = 1.18$, d) $F = 2.5 \times 10^{-4}$ M, $V_s = 1.13 \times 10^{-4}$ M s$^{-1}$. At $F = 5 \times 10^{-4}$ M, $[\text{H}_2\text{SO}_4] = 1.5$ M, the $V_s$ values for various $A$'s were: a) $A = 0.02$, $V_s = 3.4$, b) $A = 0.01$, $V_s = 1.18$, c) $A = 0.005$, $V_s = 0.38$, d) $A = 0.0025$ M, $V_s = 0.09 \times 10^{-4}$ M s$^{-1}$. At $F = 5 \times 10^{-4}$ M, $A = 0.01$ M, the $V_s$ values for various $[\text{H}_2\text{SO}_4]$ were: a) $[\text{H}_2\text{SO}_4] = 2$, $V_s = 2.3$, b) $[\text{H}_2\text{SO}_4] = 1.5$, $V_s = 1.22$. 206