

proceeds by simultaneous bimolecular and termolecular reaction paths:

$$-d(\text{Fe}^{\text{II}})/dt = k_b(\text{Fe}^{\text{II}})P_{\text{O}_2} + k_t(\text{Fe}^{\text{II}})^2P_{\text{O}_2}.$$

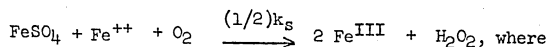
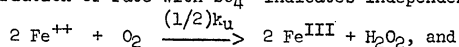
At 159°, $k_b = 1.93 \times 10^{-3} \text{ atm}^{-1} \text{ sec}^{-1}$, $k_t = 1.60 \times 10^{-3} \text{ M}^{-1} \text{ atm}^{-1} \text{ sec}^{-1}$;

the respective activation energies were measured as 13.4 (±2) and 16.3 (±2) kcal.

At 30.5°, only the termolecular path is observed (contrary to the predictions of the high temperature activation energies);

$$k_t = 2.78 \times 10^{-6} \text{ M}^{-1} \text{ atm}^{-1} (1 \text{ F } \text{H}_2\text{SO}_4).$$

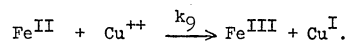
The variation of rate with SO_4^{2-} indicates independent reactions,



$$k_u = 1.4 \times 10^{-6} \text{ sec}^{-1}, \quad k_s = 3.1 \times 10^{-5} \text{ M}^{-1} \text{ atm}^{-1} \text{ sec}^{-1}, \text{ and}$$

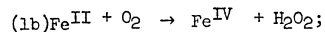
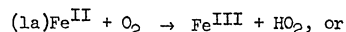
$$K_{\text{FeSO}_4} = 1.1 \text{ M}^{-1}.$$

The reaction rate increases a small amount with increasing pH. Catalysis by Cu^{++} follows the rate law $-d(\text{Fe}^{++})/dt = 4k_9(\text{Fe}^{\text{II}})(\text{Cu}^{++})$ and is probably initiated by



In 0.23 F H_2SO_4 , 0.35 F Na_2SO_4 , $k_9 = 1.9 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$.

The rate-determining step for the bimolecular path is presumably either:



for the termolecular path it is $2 \text{Fe}^{\text{II}} + \text{O}_2 \rightarrow 2 \text{Fe}^{\text{III}} + \text{H}_2\text{O}_2$.

There is evidence that the bimolecular path, the termolecular path and the Cu^{++} catalyzed path are all accelerated by complexing anions, X, and to an extent depending on the affinity of X for Fe^{+++} . Furthermore, strong complexers favor the occurrence of the bimolecular path."