

is possible catalytic activity of: Mn(II), Fe(III), Cu(II), Ni(II), and V(IV). General features of the catalyzed reaction include: (a) inhibition by oxidizable organic molecules, (b) inhibition by metal ion-complexing molecules (inorganic and organic), (c) exhibition of an induction time of several seconds to several minutes, (d) detection of metal ion - S(IV) complexes, (e) no dependence of rate on dissolved O₂ concentration, (f) dependence of the rate of the inverse of the initial H⁺ concentration (i.e., the rate is independent of pH change after the reaction has been initiated). While the catalytic reaction mechanisms are unknown, they are thought to be a modification of the initiation step of the auto-oxidation free radical mechanism (Equations 2-20 through 2-25); instead of M⁺ being a trace concentration (<10⁻⁹M) of metal ion or a reactive wall, it is a reagent present at concentrations >10⁻⁶M. The rate expressions for the various catalysts have different forms, suggesting different types of initiation mechanisms (e.g., simple redox reactions or the formation of stable, reactive complexes). The agreement between independent investigators is generally poor, indicating the likelihood of mass transfer limitations of the rate or the presence of contaminants. A large percentage of the investigations were conducted with two-phase reactors for which the mass transfer characteristics were not adequately reported; therefore, those results must be considered to be unreliable for estimating the elementary rate constant and