

The influence of inhibitors on the rate has been extensively studied by Schroeter (1963), and more recently by Altwicker (1979). According to Schroeter (1963), A and B are usually on the order of 10^{-5} molar, which means that inhibitor concentrations greater than 10^{-6} molar are effective. The form of the rate equation (Equation 89) suggests that the mechanism involves a bimolecular reaction between an inhibitor molecule and a radical in the chain.

In summary, our status of knowledge of the auto-oxidation reaction is:

1. The reaction is very slow.
2. The rate is extremely sensitive to the presence of catalysts and inhibitors.
3. The rate is first order in sulfite.
4. No reaction mechanism has been satisfactorily demonstrated to account completely for the observations of the more reliable studies (e.g., the dependence of the rate of $[H^+]^{0.5}$ found by Fuller and Crist, 1941 and by Larson et al., 1978).

It is well-established that some metal cations catalyze the oxidation of HSO_3 and SO_3^{2-} . Of particular interest to the issue of atmospheric sulfur formation in particles, mist, fog, and rain 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 O_2 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 78 through 83); instead of M^+ being a trace concentration ($<10^{-9}$ M) of metal ion or a reactive wall, it is a reagent present at concentrations $>10^{-6}$ M. The