

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 for determining the reaction order. Also, the results for investigations using supported droplets may be biased due to radical chain termination at the liquid-solid interface.

The Mn(II) catalyzed reaction kinetics have been investigated for over 75 years. The studies pertinent to the formation of sulfate in the troposphere are present in Table IX. One of the first critics of Mn(II) catalysis studies was Titoff (1903), who remarked: "in Bigelow's (1898) work the reaction occurred between two phases, and the retardation could be determined by a change in the boundary layer or by a decrease in the solution rate of oxygen." Unfortunately, that comment applies to all but three of the Mn studies in Table IX, which are: Hoather and Goodeve (1934), Neytzell-de Wilde and Taverner (1958), and Coughanowr and Krause (1965). It is odd that each of these investigators did not present rate expressions and rate constants derived from their data, and instead left to the reader the task of extracting that information. Estimates of their rate expressions are presented in Table X. There is agreement that the Mn(II) catalyzed rate is independent of dissolved  $O_2$ ,  $SO_2$ ,  $HSO_3$ , and  $SO_3^{2-}$  concentrations.

Clearly, Hoather and Goodeve (1934) and Coughanowr and Krause (1965) are in good agreement. However, Neytzell-de Wilde and Taverner (1958) observed a first-order dependence on  $[Mn(II)]$ . There appears to be no basis to discount any of the three investigations, yet it appears that serious errors may have been made. There is a slight preference for the expression for the results of Neytzell-de Wilde and Taverner (1958) because: (1) they measured the rate of disappearance of S(IV) by direct chemical means, and (2) the period of observation (10-100 minutes) of the experimental runs were sufficiently long that it is reasonable that the rate of oxidation was measured after the establishment of the radical chains, and not during the induction period.