The simple S(IV)-O_2 auto-oxidation has been the subject of numerous investigations, most of which are listed in Table VIII. The mechanism for the auto-oxidation is not firmly established. However, the behavior of the system is best explained as a modification to the scheme of Bäckström (1934), taking into account the recent results of Schmidkunz (1963) and Hayon et al. (1972):

Chain initiation,

$$SO_3^{2-} + M^+ \longrightarrow SO_3^- + M \qquad (78)$$

(M^+ = trace concentration of metal ion or reactive wall);

Chain propagation,

$$SO_3^- + O_2 \longrightarrow SO_5^- \qquad (79)$$

$$SO_5^- + SO_3^{2-} \longrightarrow SO_4^- + SO_4^{2-}; \qquad (80)$$

Oxidation,

$$SO_4^- + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_3^-; \qquad (81)$$

Termination,

$$SO_4^- + \text{inhibitor} \longrightarrow \qquad (82)$$

$$\text{radical} + \text{radical} \longrightarrow. \qquad (83)$$

Brimblecombe and Spedding (1974b) propose an alternative scheme that does not include the SO_4^- radical-ion; in their scheme, equation (80) is replaced by:

$$SO_5^- + SO_3^{2-} \longrightarrow SO_3^- + SO_5^{2-}, \qquad (84)$$

$$SO_5^{2+} + SO_3^{2-} \longrightarrow 2\ SO_4^{2-}, \qquad (85)$$

and equation (82) is absent.

Hegg and Hobbs (1978) have discussed most of the investigations identified in Table VIII, and they summarized the rate expressions, rate constants, and important features of the studies. The observations can be classified into three types of rate expressions: