2.3.4.1 S(IV)-O_2 - H_2O System-- The simple S(IV) - O_2 auto-oxidation has been the subject of numerous investigations, most of which are listed in Table 2-5. 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

$$SO_3^{2-} + M^+ \rightarrow .SO_3^- + M \qquad (2\text{-}20)$$

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

Chain propagation

$$.SO_3^- + O_2 \rightarrow .SO_5^- \qquad (2\text{-}21)$$

$$.SO_5^- + SO_3^{2-} \rightarrow .SO_4^- + SO_4^{2-} \qquad (2\text{-}22)$$

Oxidation

$$.SO_4^- + SO_3^{2-} \rightarrow .SO_4^{2-} + SO_3^- \qquad (2\text{-}23)$$

Termination

$$.SO_4^- + \text{inhibitor} \rightarrow \qquad (2\text{-}24)$$

$$\text{radical} + \text{radical} \rightarrow$$

Brimblecombe and Speeding (1947b) propose an alternative scheme that does not include the $.SO_4^-$ radical-ion; in their scheme, equation (2-22) is replaced by:

$$.SO_5^- + SO_3^{2-} \rightarrow .SO_3^- + SO_5^{2-} \qquad (2\text{-}26)$$

$$.SO_5^{2+} + SO_3^{2-} \rightarrow 2\ SO_4^{2-} \qquad (2\text{-}27)$$

and equation (2-24) is absent.

Hegg and Hobbs (1978) have discussed most of the investigations identified in Table 2-5, and they summarized