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# Manganese-Catalyzed Sulfite Oxidation as a Synergism between Manganous Ions and Unavoidable Traces of Iron

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Energy production strongly affects the environment, in particular, to the increase of the atmospheric loads of acidic gases. During the past years great strides have been spent toward understanding aqueous-phase chemical reactions in cloud droplets, in particular, those involved transition metal ions. Current understanding of $SO_2$ oxidation catalyzed by manganese ions yet not well determined. The appearance in the literature of a one-term rate laws including a zero or square terms in Mn(II) has served as a motive to postulate formation of manganese(II) hydrogen sulfite complex or an oxo- (or hydroxo-) bridged mixed-valence complexes which not to be identified experimentally.

Our experiments as well as a thorough review of experimental and interpretive papers of the earlier studies of the catalytic reaction led to the conclusion that the process represents a synergism between manganese ions and residual iron. This iron present even in amounts of single-digit-10-8 M range gives the start of the chain reaction in a step $FeOH_2+$ + $HSO^{3-}$ - $Fe^{2+}$ + $SO^{3-}$ + $H_2O$. The same initiation involving manganese ions is thermodynamically forbidden thus indicating that these ions itself catalytically inefficient. Its activation occurs with the only assistance of iron, but being activated by a such manner the Mn(II) can strongly shift iron's partitioning between its valence states to its oxidized form.

The $SO^{3-}$ radicals arisen in the initiation step are rapidly converted into $SO^{5-}$ which enter in the chain-carrier cycle $SO^{5-}$ + Mn(II) - $HSO^{5-}$ + Mn(III); Mn(III) + $HSO^{3-}$ - Mn(II) + $SO^{3-}$ + $H^3$ thus providing sulfite depletion. The cycle is interrupted when the chain-carriers are interacted. The rate law of the overall process depends on which steps $SO^{5-}$ + Mn(II) or Mn(III) + $HSO^{3-}$ appear as the limiting stage of which rates depend on pH, [Mn(II)]/[S(IV)]. Such a view enables examination of those conditions under which the limitation to the rate of the catalytic reaction is controlled by the reaction involving $SO^{5-}$ (second-order in Mn(II)) or Mn(III) (zero-order in Mn(II)). Readily applicable kinetic criteria are given to delimit the conditions. On the whole, a fairly coherent picture emerges when existing experimental data are compared with those predicted on the basis of a concept about “a synergism between manganese and residual iron”.

Within the mechanism it becomes clear that manganese ions doubly affect the rate of sulfite depletion: (i) these ions are involved in the chain-carriers cycle and (ii) they shift the balance between Fe(III) and Fe(II) toward to ferric ions thus increasing the rate of chain initiation as a result of sharp rising in concentrations of Fe(II) oxidants. The estimated synergistic coefficient between manganese ions and residual iron is up to 105!

Preliminary impact of manganese ions on $SO_2$ depletion in the troposphere and on iron's partitioning in cloud droplets have been analyzed within home built box model.

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