



Iron Catalysis of SO₂ Oxidation in Cloud Droplets

Igor Larin and Alexander Yermakov

Institute of Energy Problems of Chemical Physics of the Russian Academy of Sciences, Chemical Physics of the Atmosphere, Moscow, Russian Federation (iklarin@narod.ru, 8(495)1378258)

What can happen to solution of a sulfite saturated by oxygen if a small amount of Fe(III/II) is introduced? The normally slow autooxidation is specifically accelerated by these ions. That is why iron-catalyzed oxidation of sulfite is of great interest for atmospheric chemistry. In general, the kinetics of the reaction is characterized by bad a reproducibility. The reaction orders vary unpredictably between zero – second order both in sulfite and in iron. None of the data support the half-order dependence on iron ion concentration expected for radical-radical recombination. All these “anomalies” receive a naturally explanation assuming a conjugation between the branching reaction, $\text{HSO}_5^- + \text{Fe}^{2+} \rightarrow \text{FeOH}^{2+} + \text{SO}_4^-$ and those producing HSO_5^- in the chain-carriers cycles $\text{SO}_5^- + \text{HSO}_3^- / \text{SO}_3^{2-}$ and the metal cycle $\text{SO}_5^- + \text{Fe}_{aq}^{2+}$. Being coupled these steps are able to accelerate or to slow down significantly the production of chain-carriers at certain concentration conditions or exposures to any additives. Perhaps most importantly is also that the radical-radical recombination $\text{SO}_5^- + \text{SO}_5^-$ represents a gross but not a net loss of the chain-carriers, because nearly all of them are reformed through the branching step $\text{HSO}_5^- + \text{Fe(II)} \rightarrow \text{FeOH}^{2+} + \text{H}_2\text{O} + \text{SO}_4^-$ and $\text{SO}_4^- + \text{HSO}_3^- + \text{O}_2 \rightarrow \text{SO}_5^-$. In the report the result of the modeling of the gas-phase/aqueous-phase reactions of SO₂ removal from the gas are given.

This work was supported by Russian Fund of Basic Research (## 08-05-00818-[U+FFFD]9-05-00270-[U+FFFD]nd by the Presidium of the Russian Academy of Sciences through program no. 4, "Changes in the Environment and Climate—Natural Disasters." which are gratefully acknowledgement