The Role of Iron and Copper Species for Reactions of Photooxidants and Photochemical Reactions in Atmospheric Waters

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In cloud and fog droplets, iron and copper species can undergo photochemical reactions and chemical reactions that control the rate of mass transfer of HO$_2$ from the gaseous phase. Though it is clear that the complex aqueous-phase reactions of iron and copper affect the concentrations of photooxidants and pollutants in the troposphere, the reactions can only be accurately modelled when an improved understanding of the individual reactions of dissolved transition metals becomes available. To better describe and quantify the different reactions controlling chemical processes in the aqueous phase, we have determined rate constants for several critical reactions and evaluated the importance of the reactions under typical atmospheric conditions. The research program in our laboratories related to the HALIPP project has so far covered the following steps:

1. Further information has been compiled on the concentrations and speciation of transition metals and chelating organic compounds in atmospheric waters. Our review of available data indicates that dissolved iron is generally present in the nanomolar to micromolar range in rain and in the micromolar to millimolar range in fogwater. A large fraction of the dissolved iron is present as reduced iron (II). Copper is usually present at concentrations in the range of 1-10% of that of the total iron. The dominant chelating organic compound appears to be oxalic acid. Its concentration is often in the same range as reported for dissolved iron. A summarizing figure illustrating recently reported concentrations of iron, copper and oxalic acid in rain and in fogwater is presented in Sedlak and Hoigne (1993).

2. Photochemical reactions of iron occurring in the absence and in the presence of oxalic acid have been studied in detail (Faust and Hoigne, 1990; Zuo and Hoigne, 1992). These experiments were performed using model solutions exposed in quartz tubes to either sunlight or filtered light from a mercury lamp in a merry-go-round reactor. The results show that during daytime, dissolved iron (III) is photoreduced to iron (II) and the ligands are oxidized. If only the aquo complex (FeOH$_2^+$) is considered, the photolysis is relatively slow, but leads to the
formation of OH radicals. The photolysis is accelerated when iron is chelated by oxalate. For oxalate-complexed iron to be important to iron photochemistry, oxalic acid has to be present at concentrations > 0.1 µM—a concentration which is often observed. Chelation by oxalate acts as an efficient electron donor for the photoreduction of the metal ion. By this process, atmospheric oxalic acid is efficiently oxidized to CO₂, through several steps, including one in which an O₂ is reduced to HO₂/O₂⁻. In closed aqueous systems, HO₂/O₂⁻ reacts with iron (III) to form hydrogen peroxide and complete the iron redox cycle. The pathway of this cycle is shown in Figure 1. The pathway is rather different from that occurring at high concentrations of iron and oxalate typically employed for ferrioxalate actinometry, where an intermediate oxalate radical is further oxidized by iron (III) oxalate instead of by oxygen. The rate of photolytic degradation of oxalate, and the corresponding formation of hydrogen peroxide varies with the concentration of iron (III). In September noon sunlight, 5 to 10 µM of oxalate was photolytically degraded within 14 minutes in the presence of 1 µM iron (III). The rate of photolytic conversion, however, decreased at lower iron concentrations. The fact that much more oxalate was degraded than the amount of iron present confirms the involvement of a chain reaction in which iron is cycled between oxidation states. By using known reaction rate data, we predict that in atmospheric water droplets iron (II) is reoxidized by HO₂/O₂⁻ (daytime process) or ozone or hydrogen peroxide (nighttime processes). The rates of the different reactions leading to iron (II) oxidation are compared in Figure 2.

3. To learn more about the redox cycling of iron and copper in atmospheric waters and the effect of HO₂/O₂⁻ on the cycle, solutions of dissolved iron (II) and iron (III) were exposed to gamma radiation in the presence of oxalate and traces of copper (Sedlak and Hoigne, 1993). Gamma radiation ionizes water molecules into primary species, which are quickly converted into HO₂/O₂⁻ in the presence of oxygen and 1mM formate. When an radiation intensity corresponding to a HO₂/O₂⁻ production rate of approximately 60 nM/s was used, iron cycled between the iron (II) and iron (III) forms through reactions with HO₂/O₂⁻, and reached an equilibrium in approximately two minutes (Figure 3). Final iron (II) concentrations increased linearly when copper was increased from 10 to 50 nM. Higher Fe(II) concentrations were observed because Cu(II) reacts with HO₂/O₂⁻ to produce Cu(I), which can reduce Fe(III). The catalytic effect of copper on Fe(II) does not decrease with time, even when copper cycles thousands of times between its different oxidation states. However, when oxalate is present, Fe(III) reduction is negligible, because oxalate-chelated Fe(III) does not react with either
HO$_2$/O$_2^-$ or Cu(I). The iron (III)-oxalate complexes do, however, undergo photolysis (see above).

4. Copper is probably the dominant sink for HO$_2$/O$_2^-$ in cloudwater. It is difficult to assess the copper redox cycle because literature values of the rate constant for the reaction of HO$_2$/O$_2^-$ with copper (I) and copper (II) vary by over an order of magnitude. We have therefore determined the value using pulse radiolysis combined with kinetic spectroscopy. Values included in Figure 4 result in the most consistent simulation of the time dependent concentration of transients observed by kinetic UV spectroscopy (von Piechowski et al., 1990). These nearly diffusion controlled rate constants indicate that dissolved copper is the dominant sink for HO$_2$/O$_2^-$ even when it is only present in the nanomolar concentration range.

Conclusions:
During daytime, both the photolysis of iron (III)-oxalato complexes as well as the reduction of Fe (III) aquo complexes by HO$_2$/O$_2^-$ (often mediated by copper (I)-(II) acting as a catalyst) occur much faster than reoxidation reactions. Therefore, most of the dissolved iron in atmospheric waters should be observed in the iron (II) state. At night, the reductive reactions stop, and iron is reoxidized by hydrogen peroxide and ozone.

At concentrations of copper and iron comparable to those observed in rainwater, copper and iron serve as the dominant sinks for HO$_2$/O$_2^-$.

The rapid rates of these reactions result in faster transfer of HO$_2$ into cloud droplets and enhanced rates of hydrogen peroxide production. Although all of the reactions and rate constants of the iron and copper cycles have not yet been fully evaluated, it is clear that these transition metals are very important to the transformation of photooxidants and pollutants in atmospheric waters.

Literature Cited:


Figure 1. Scheme of photochemical cycling of iron in the presence of oxalate (Ox) showing the iron-catalyzed photooxidation of oxalate and the formation of hydrogen peroxide. The rates for the transformations occurring in the aqueous phase have been used for the estimate of the rate of transformation occurring in the cloud system by accounting for the in-cloud liquid water content of 0.3 g/m$^3$. Figure from Hoigne et al., 1993; adapted from Zuo and Hoigne, 1992.
Figure 2. Summary of main backreactions for the reoxidation of iron (II) in atmospheric waters. Assumed concentrations of reactants (numbers above arrows [ ] in M units) approximate those considered by Lelieveld and Crutzen (1991) or Chameides and Davis (1982). The given second-order rate constants (numbers below arrows ( ) ) are rounded values (M⁻¹ s⁻¹) from literature. For references see Hoigné et al., 1993, or Sedlak and Hoigné, 1993).
Figure 3. Summary of main reactions by which aqueous O$_2^-$ is transformed in atmospheric waters. Assumed concentrations of reactants (numbers above arrows [ ] given in M units) approximate those considered for summer daytime by Lelieveld and Crutzen (1991) or Chameides and Davis (1982). The given second-order rate constants (numbers below arrows ( )) are rounded values (M$^{-1}$ s$^{-1}$) from literature. For references see Hoigne et al., 1993, or Sedlak and Hoigne, 1993).

Figure 4. Percentage of iron as iron (II) after exposure to gamma radiation in the presence of trace concentrations of copper.