

The role of transition metal ions on oxyhalogen redox reactions

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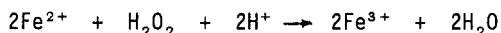
Abstract - The details of some of the reactions and interactions of many of the oxyhalogen species are reported in the literature. The formation of highly reactive, complex intermediates is common-place in these reactions. However, the role of metal ions on the decomposition of these intermediates is less well understood. Their role is also of primary importance in understanding the microscopic details of most oscillating reactions where non-metal to transition metal electron transfer reactions play a pivotal role.

The reaction between chlorite ion and chlorine and/or hypochlorous acid to form the highly reactive Cl_2O_2 intermediate is very rapid in acid solution followed by the primary production of chlorine dioxide and under somewhat more dilute conditions reasonable concentrations of chlorate ion. In less acidic solutions, the principal pathway involves the formation of chlorate ion by means of direct electron transfer between transition metal species and the chlorine containing intermediates. In the absence of transition metal ions in the near neutral pH range, the reaction proceeds negligibly slow.

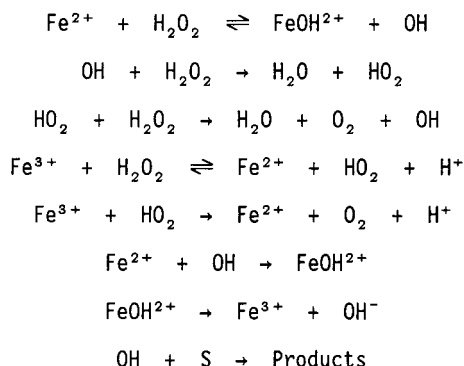
Emphasis will be on the role of transition metal ions in one- and two-electron transfer reactions in redox processes involving highly reactive non-metal species.

INTRODUCTION

The decomposition of hydrogen peroxide in the presence of transition metal ions demonstrates the role and importance of specific free radical species. Fenton's reagent is obtained by mixing aqueous iron(II) and hydrogen peroxide which is a stronger oxidizing agent than hydrogen peroxide alone (ref. 1). It can oxidize dihydrogen, initiate polymerization and oxidize organic substances that are difficult to oxidize. In the absence of a substrate, the overall reaction



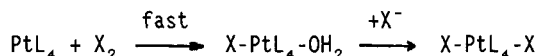
is accompanied by catalytic decomposition of hydrogen peroxide. This, however, does not explain the enhanced oxidizing power. The explanation is clear only after the overall reaction has been analyzed into simpler reactions:



where S denotes the substrate to be oxidized (e.g., H_2) and Products denotes the products of the reaction. Depending on the pH, further reactions can be written involving HO_2^- and O_2^- which are derived by proton loss from H_2O_2 and HO_2 . Even these reactions may be

generally analyzed in more detail, but even this limited analysis alone indicates that the enhanced oxidizing power of Fenton's reagent is due mainly to the intermediate OH radicals which are generated as a result of the $\text{Fe}^{2+} - \text{Fe}^{3+}$ couple acting as a one-electron redox couple.

The oxidation of square-planar complexes of platinum(II) by chlorine or bromine in aqueous solution results in a trans-dihalo platinum(IV) complex as a final reaction product. This is a classical method used to prepare platinum(IV) complexes which involves the oxidative addition of dihalogen to the platinum(II) complex as is shown below (ref. 2-5):



Aqueous solutions of chlorine contain Cl_2 and HOCl in equilibrium. Both of these molecules oxidize platinum(II) complexes quantitatively. However, in general the oxidation by Cl_2 is orders of magnitude faster than that by HOCl although frequently different reaction products are observed.

Another point of mechanistic interest in halogen reactions is the relative reactivity of X_2 and X_3^- when they oxidize a common reducing agent. In most cases the halogen itself is the better oxidizing agent with the difference in rate generally being due to differences in the activation enthalpies. A rich diversity of metal ions have been studied as reductants including transition metal ions such as iron, cobalt, manganese and copper and other metal ion species containing f electrons such as europium(II) and uranium(IV) (ref. 6-9). In general, the question of inner sphere versus outer sphere mechanism has only been resolved in a few of the halogen reactions in that the obstacles include lability of the final products and the possibilities that the reactions may proceed by a series of uni-valent changes.

On the other hand, reactions of the oxyhalogen species are not very well documented in text books except for the disproportionation reactions of chlorine to form hypochlorous acid and chloride ion or that of iodine where iodate ion is readily formed at room temperature (ref. 10-12). However, the chemistry of species such as chlorine dioxide, chlorite ion, bromate ion and bromine dioxide receive considerable attention in the literature because of the ease with which they undergo electron transfer/oxidation reduction reactions.

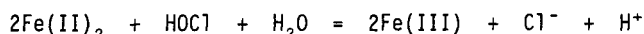
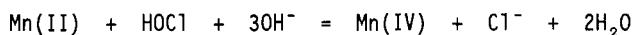
OXYHALOGEN INTERMEDIATES

The oxyhalogen species -- bromate, iodate, or chlorite ion -- are indispensable constituents of all known homogeneous isothermal chemical oscillators in solution (ref. 13-19). Although the first oscillating reaction reported, the Bray-Liebhafsky reaction (ref. 13), is an iodate ion system, the overwhelming majority of oscillators reported to date contain either bromate ion or chlorite ion.

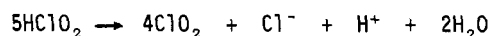
Bromate ion oscillators have been by far the most thoroughly studied and characterized -- with the Belousov-Zhabotinskii system, which was discovered almost thirty years ago, becoming the best understood prototype with extensive bodies of experimental and theoretical work which are in remarkably good agreement. In general, our understanding of chlorite ion oscillators is at a more primitive stage in that these systems were first reported less than ten years ago. Invariably, these highly complicated redox systems involve species such as XO_2 , HXO_2 , HOX , X_2 and X^- along with various metal ions. Clearly, the role of inner sphere versus outer sphere substitution reactions and the corresponding one-electron versus two-electron transfer processes play an important part in a detailed explanation of these systems (ref. 20-26).

For that reason, some comment with respect to the reactions and interactions of the chlorine containing oxyhalogen species is appropriate in order to appreciate the complexity of the detailed mechanism associated with the examples cited above.

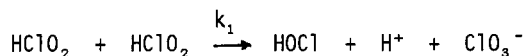
Chlorine is a strong oxidizing agent and reacts with a wide variety of compounds and in particular those that are considered reducing agents. The following reactions are typical of the reactions which occur between chlorine and inorganic reducing materials. However, it should be noted that the actual reactions (in terms of stoichiometry, kinetics and detailed mechanisms) are generally considerably more complex than the illustrations:



The acid catalyzed disproportionation of chlorous acid has been studied under a variety of pH values and ionic strengths (ref. 11, 27-30). Hydrogen ion affects the rate of chlorine dioxide production giving rise to the overall stoichiometry:

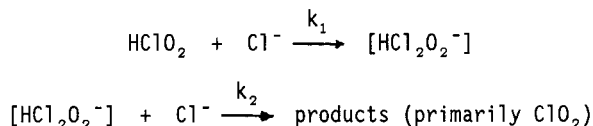


At pH 2.5 about 20% of the chlorite ion undergoes disproportionation in less than 10 minutes. Schmitz and Rooze (ref. 31) have clearly shown that chlorate ion is formed from the acid catalyzed disproportionation of chlorite ion only as a result of impurities such as ferric ion. Furthermore, they have shown that the reaction:



is not an elementary reaction in the decomposition of acid solutions of chlorite ion.

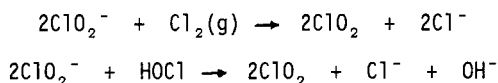
In acidic solutions (pH less than 3), the principle pathway for the formation of chlorine dioxide is catalyzed by chloride ion:



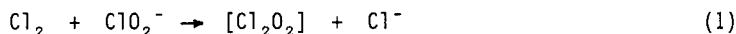
In other words, in acid solution, hydrogen ion and chloride ion and various transition metal ions enhance the formation of ClO_2 from the disproportionation of chlorite ion.

Chlorine and/or hypochlorous acid readily oxidize chlorite ion to form chlorine dioxide. On the other hand, in dilute solution, mostly chlorate ion is formed with the formation of little or no chlorine dioxide. In acid solution, these reactions occur on the seconds time scale. However, at pH 7 with solutions containing 1 mg/L of each reactant, the half-life is reported to vary from many hours to days, possibly depending on the chloride ion concentration. Trace amounts of ferric ion enhance the rate such that even in neutral solution the reaction is completed in just a few seconds.

The stoichiometry of chlorine dioxide formation from the reaction of excess aqueous hypochlorous acid or gaseous chlorine with dissolved chlorite ion is as follows:



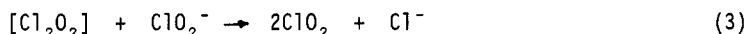
These reactions involve the formation of the unsymmetrical intermediate Cl_2O_2 :



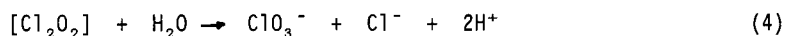
At high concentrations of reactants, the intermediate is formed very rapidly. Chlorine formed in Eqn. 2 is recycled by means of Eqn. 1. Thus, primarily chlorine dioxide is produced as a result.



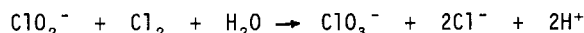
or



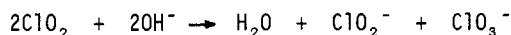
On the other hand, at low initial reactant concentrations of both reactants, primarily chlorate ion is formed due to the first order decomposition of the Cl_2O_2 intermediate:



Thus, high concentrations favor the second order reactions (Eqns. 2, 3) and chlorine dioxide is formed. At low concentrations, the second order process becomes unimportant and the first order reaction (Eqn. 4) produces chlorate ion rather than chlorine dioxide. The reasons are clearly related to presence of high concentrations of initial reactants and the rapid formation of the Cl_2O_2 intermediate which in turn is responsible for the formation of chlorine dioxide.



Chlorine dioxide disproportionates in base by the reaction:

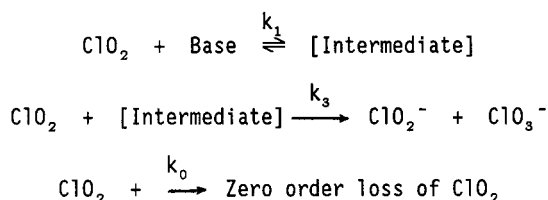


At 20°C with an initial hydroxide ion concentration of 1×10^{-2} M the rate law reduces to:

$$-d[\text{ClO}_2]/dt = 0.0017[\text{ClO}_2] + 10.0[\text{ClO}_2]^2$$

If the initial chlorine dioxide concentration is 1×10^{-3} M, 85% of the total rate of decomposition occurs via the pathways given by the second-order term of the rate law.

The base disproportionation of chlorine dioxide is dependent not only on the chlorine dioxide and hydroxide ion concentration but also the presence of other bases such as phosphate ion, carbonate ion, borate ion, and a wide variety of metal complexes. These reactions are fast and clearly complicate our understanding of the details of the electron transfer steps and the role of metal ions in the disproportionation process:



Thus at high concentrations of chlorine dioxide the process becomes pseudo first order in chlorine dioxide and markedly dependent on the concentration and type of base or anion and/or metal complex present in the solution under consideration.

Halperin and Taube (ref. 32) conducted oxygen-18 atom tracer experiments on the base decomposition of chlorine dioxide during the formation of chlorate ion and chlorite ion. The isotopic composition was almost identical with the original chlorine dioxide although minor dilution by solvent oxygen was observed. By using the rate law as previously reported by Bray (ref. 27), they proposed that there existed an unsymmetrical configuration of $[\text{ClO}_2]_2$ in the transition state as shown below:



According to Halperin and Taube, the hydroxide ion would preferably attack the more positive chlorine such that in the majority of cases the solvent oxygen would reside in the chlorate ion product. If in a small percentage of events the hydroxide ion attacked the +1 chlorine, a small amount of solvent oxygen would be observed in the chlorite ion product.

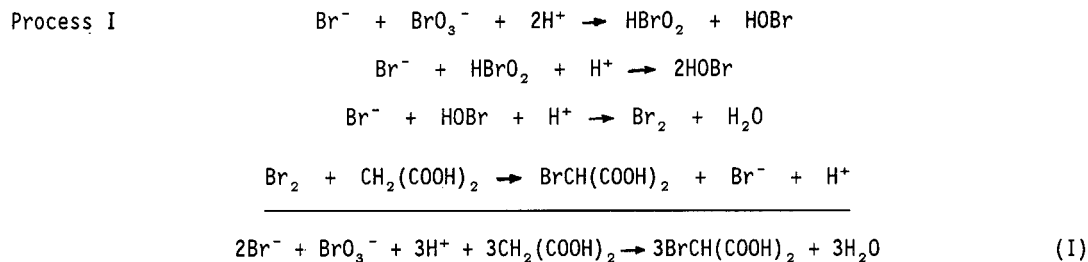
The reduction of chlorine dioxide by iodide ion occurs rapidly in basic solution, producing chlorite ion, which is reduced only very slowly under neutral conditions. However, at low pH values (i.e. pH < 2) chlorite ion and chlorine dioxide are both rapidly reduced by iodide ion. Iodine (and the accompanying triiodide ion) is formed in each case. In all cases, most transition metal ions catalyze these processes (ref. 11, 20-31).

OSCILLATING REACTIONS

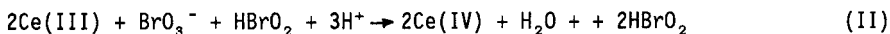
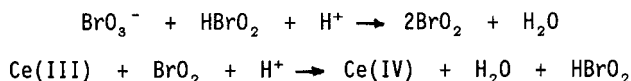
Interestingly enough, the reactions and interactions of the various oxychlorine species are the best understood of all of the oxyhalogen reactions. In this context, it is not surprising that this lack of a detailed understanding of the interaction of the oxyhalogen species themselves has led to considerable difficulty in totally understanding the mechanism of oscillating reactions.

One of the best examples is the Belousov-Zhabotinskii (ref. 14-19) reaction in that it illustrates some very unusual chemical behavior and because its total elucidation provides both a chemical challenge to obtain the necessary thermodynamic and kinetic information about the various species and a computational challenge to simulate the experimental results.

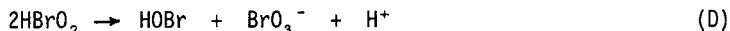
The Belousov reaction mechanism can be best understood by recognizing there are two different overall processes that can occur in the system. There is little cross-talk between the two processes because one involves only singlet species and the other is basically a radical process as is shown below:



Process II



and



Above a certain critical bromide ion concentration, Process I occurs while below this critical bromide ion concentration Process II is dominant. Oscillations occur because Process I consumes bromide ion and thus inevitably leads to the onset of Process II which by indirectly producing bromide ion, returns the system to control by Process I.

The rate determining step for Process I is the reduction of bromate ion by bromide ion through a series of oxygen transfer or two-electron processes. Furthermore, none of the singlet oxybromine species present during Process I are thermodynamically plausible as single electron oxidants such as are required to oxidize cerium(III) to cerium(IV). Thus, very little oxidation of cerium(III) to cerium(IV) occurs during Process I.

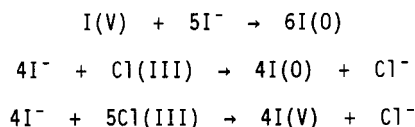
At low bromide ion concentrations, the system shifts to Process II where bromate ion and bromous acid produce BrO_2 which behaves very similarly to ClO_2 . The products are HBrO_2 and cerium(IV). The non-linear kinetic behavior of Process II provides the feedback that is one of the requirements for the sustained oscillatory behavior.

Subsequently, it has been shown that manganese(II) and iron(II) behave similarly in that they also involve one-electron transfer processes. However, the reduction of bromate ion by potentially multi-equivalent reducing agents such as Br^- , H_2O_2 , HN_3 , and vanadium(II) result in simple, mixed second order rate laws which exhibit no induction periods. Clearly, the distinction between one-electron and two-electron transfer processes determine the oscillatory behavior of the bromate system.

The chlorite ion oscillators provide an even larger diversity of oxychlorine intermediates and more complications in unravelling the details of the individual mechanistic processes. Our understanding becomes even more limited when iodide ion and/or iodate ion are also involved.

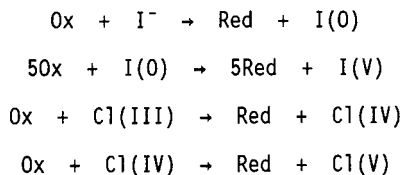
A preliminary classification scheme can be proposed in view of the observation that $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^- , H_3AsO_3 , and Fe(CN)_6^{4-} also show oscillatory behavior in the ClO_2^- -- I^- and ClO_2^- -- IO_3^- systems.

The major overall processes taking place in systems containing chlorite ion, iodide ion, iodine and/or iodate ion appear to be the following (ref. 33):



The details of these individual reactions have been well studied and a fairly extensive body of experimental data and mechanistic speculation is available for these processes.

If, in addition to chlorite ion and iodide ion, a system contains a one-electron oxidizing substrate (designated Ox) then the following processes may also be expected to occur:



where Red represents the reduced form of the species Ox.

Clearly, even this simplified stoichiometry neglects kinetically important oxyhalogen species such as HOCl , Cl_2O , and Cl_2O_2 which have been shown to be important in the corresponding disproportionation and redox reactions of chlorite ion and chlorine dioxide.

In many ways, our understanding of the oxyhalogen oscillatory systems is greatly hampered by the lack of detailed information available on interactions between the oxyhalogen species themselves. Most likely, the rate laws which have been published correctly describe the broad features of the reactions, but they do not correctly describe the microscopic details of the individual reactions actually involved in the one- and two-electron transfer processes which cause or eliminate the oscillatory behavior.

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