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CHAPTER 62

The Chemistry of Oxo-Chlorine Compounds Relevant to Chlorine Dioxide Generation

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Within the last decade, halogenated organic compounds formed in drinking water by disinfection with chlorine have caused considerable concern throughout the drinking water industry.¹ The U.S. Environmental Protection Agency (EPA) has regulated the concentration of THMs to a maximum of 100 $\mu\text{g}/\text{L}$ total THMs in drinking water as a first step in an effort to control the chlorinated organic compounds formed during the disinfection process. Three strategies for meeting this regulation are removal of the organic precursors; removal of the THMs that are formed; or substitution of an alternative disinfectant that does not form THMs.

One of the alternative disinfectants that has received considerable attention is chlorine dioxide (ClO_2), which offers several attributes that make it an acceptable substitute for chlorine.² It does not form THMs. It does, however, produce some chlorinated organic compounds in aqueous solution, but under conditions encountered in drinking water treatment the concentrations of these compounds are 10 to 100 times less than the concentration produced by chlorine under the same conditions.³ Chlorine dioxide is an effective disinfectant over a broad pH range and in some cases significantly more effective than chlorine.⁴ Chlorine dioxide can be measured easily at the point of use of the disinfected water, permitting residual disinfectant measurements to be used as an indicator of the microbiological safety of the delivered water.

Chlorine dioxide is an unstable explosive gas at concentrations greater than about 10% in air.⁵ The gas, either pure or in mixtures, cannot be compressed and stored; hence, ClO_2 must be generated on-site for immediate use. For drinking water treatment, ClO_2 is most commonly generated by the oxidation of sodium chlorite by chlorine.

This chapter reviews the chemistry of oxo-chlorine compounds so that the reactions used to generate ClO_2 for water treatment may be more fully understood. This chapter also includes results from our research on the kinetics of the oxidation of sodium chlorite by chlorine. This reaction is the preferred ClO_2 generation reaction for water treatment, because of the high yields that can be achieved and because there are no waste streams that pose disposal problems.

AQUEOUS CHEMISTRY OF CHLORINE AND OXO-CHLORINE COMPOUNDS

Table I lists the major chlorine compounds of the oxo-chlorine family and their oxidation states.

Chlorine Hydrolysis Reaction

Chlorine gas is moderately soluble in water. In addition to solvated halogen molecules, hypochlorous acid and chloride ion are present in aqueous solution due to the hydrolysis/disproportionation reaction of the solvated molecular chlorine. These reactions are



The chlorine hydrolysis constant is given by

$$K_{\text{H}} = \frac{[\text{HOCl}] [\text{H}^+] [\text{Cl}^-]}{[\text{Cl}_2(\text{aq})]} \quad (3)$$

The rate of chlorine hydrolysis has been widely studied. The interpretation of the results from early studies was complicated because of confusion about the mechanism of the chlorine hydrolysis reaction. Shilov and Solodushenkov⁶ assumed the reaction to be as shown by Equation (2). Their results, however, indicated that the rate constant decreased as the reaction proceeded. Morris⁷ recalculated the results of Shilov and Solodushenkov,⁶ assuming the reaction involved the hydroxide ion

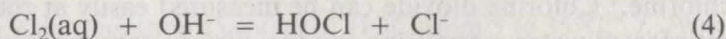


Table I. Chlorine and Oxo-Chlorine Species

Oxidation State	Oxidation No.	Compounds	Name
Chlorine (-I)	-1	HCl, Cl ⁻	Hydrochloric acid, chloride
Chlorine (0)	0	Cl ₂	Molecular chlorine
Chlorine (I)	1	HOCl, OCl ⁻	Hypochlorous acid, hypochlorite ion
Chlorine (III)	3	HClO ₂ , ClO ₂ ⁻	Chlorous acid, chlorite ion
Chlorine (IV)	4	ClO ₂	Chlorine dioxide
Chlorine (V)	5	HClO ₃ , ClO ₃ ⁻	Chloric acid, chlorate ion
Chlorine (VII)	7	HClO ₄ , ClO ₄ ⁻	Perchloric acid, perchlorate ion

and found much better constancy in the calculated second-order rate constant. The value of the second-order rate constant determined by Morris was $5 \times 10^{14} M^{-1} s^{-1}$, an extremely high value. The Morris⁷ calculations also indicated zero activation energy for the chlorine hydrolysis reaction. A reinvestigation of the chlorine hydrolysis reaction by Shilov and Solodushenkov⁸ did not reproduce the decreasing rate constant observed in their first study, so that Morris' argument did not seem to apply. Lifshitz and Perlmutter-Hayman⁹ tried to establish which of Equations (2) or (4) represented the hydrolysis in pure water. Their findings supported the original assumption of Shilov and Solodushenkov⁶ that Equation (2) correctly represented the chlorine hydrolysis reaction in pure water. Furthermore, Lifshitz and Perlmutter-Hayman⁹ pointed out that the maximum second-order rate constant to be expected in solution corresponded to the diffusion-controlled limit of $1 \times 10^{10} M^{-1} s^{-1}$, a much lower value than that calculated by Morris,⁷ and that the rate of formation of hydroxide ions was not rapid enough in acid solution for Equation (4) to contribute significantly to the rate of chlorine hydrolysis.

Morris'⁷ ideas relating to the mechanism of chlorine hydrolysis were not totally in error, however, as later demonstrated by Spalding.¹⁰ The equilibrium pH of a chlorine solution in pure, unbuffered water at a given temperature is controlled by the total chlorine concentration of the system, as given by the chlorine hydrolysis equilibrium constant, Equation (3). In the studies of Shilov and Solodushenkov^{6,8} and of Lifshitz and Perlmutter-Hayman,⁹ chlorine gas was dissolved in pure, unbuffered water so that the pH of the reaction solution was near pH 2 and may have been somewhat lower at the lower temperatures of these studies. Eigen and Kustin¹¹ proposed a general mechanism for the hydrolysis of halogens, including chlorine. Both Equations (2) and (4) are included in the general mechanisms. Eigen and Kustin's¹¹ results indicated that at pH 2.2, the highest pH they investigated, the hydrolysis mechanism represented by Equation (4) did not contribute to the rate of chlorine hydrolysis. Spalding,¹⁰ however, absorbed chlorine gas into water at initial pH values between 3 and 10.2. His results indicated that below an initial pH of 10.2, the primary reaction mechanism for the hydrolysis of chlorine was that given in Equation (2); however, above pH 12.5, the reaction mechanism was that proposed by Morris,⁷ which is given in Equation (4). It should be emphasized that the actual pH value reported by Spalding,¹⁰ at which Equation (2) became dominant, was the initial pH of the absorbing fluid and that the contact time was very short. Under different experimental conditions this pH value might be shifted. Spalding¹⁰ estimated the first-order chlorine forward rate constant for Equation (2) to be $20.9 s^{-1}$ at $25^{\circ}C$. His estimate for the second-order rate constant of Equation (4) was $1 \times 10^6 M^{-1} s^{-1}$ at $25^{\circ}C$. More recent work by Sandal et al.,¹² who studied the absorption of chlorine gas in strong sodium hydroxide solution, gave a value for the second-order rate constant of Equation (4) as $2.7 \times 10^7 M^{-1} s^{-1}$ at $0^{\circ}C$.

Figure 1 shows a comparison of the first-order forward rate constants for the chlorine hydrolysis reaction determined in our laboratory with the results

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