Chapter 2
Web Text Box 4

HOCl, an acid and an oxidizing agent

Chlorine bleach is a solution of sodium hypochlorite, NaOCl. This is an ionic compound and in water exists as Na^+ and OCl^- ions. Hypochlorite is the deprotonated form of hypochlorous acid HOCl, which is a very weak acid: its pK_a is 7.53. Thus in the NaOCl solution some of the hypochlorite ions grab an H^+ from water, leaving OH^- behind. The result is that the solution is alkaline: usually about pH 11, although more concentrated solutions have an even higher pH.

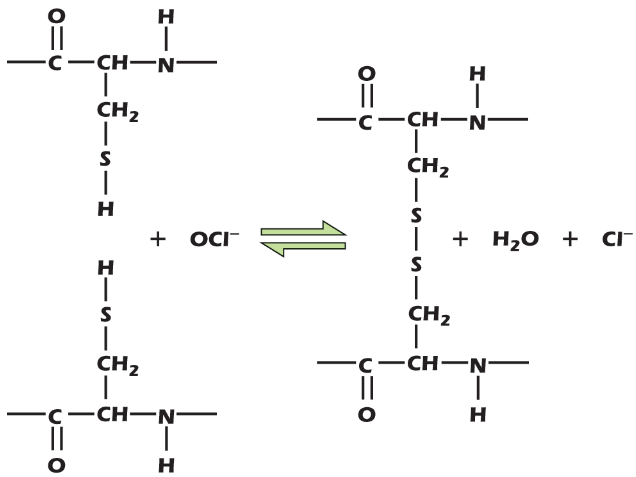
You should be able to calculate what fraction of the total hypochlorite is protonated at pH 11: check that you can!

Try the calculation yourself, then check the answer in the box below!

The pK_a of hypochlorous acid HOCl is 7.53. What percentage of the total hypochlorite is protonated at pH 11.0; that is, calculate the value of

$100 \times [HOCl] / ([HOCl] + [OCl^-])$?

Although HOCl is a very weak acid the hypochlorous ion is a strong oxidizing agent and will readily give up the oxygen atom leaving a simple chloride ion Cl^-. One of the chemical groups that it attacks is the –SH side group on the amino acid cysteine. Two cysteine side chains are oxidized and form a disulfide bond:



Chlorine bleach: an illustration of acid/base and oxidation/reduction reactions

The cysteines have been oxidized because they have lost hydrogen atoms. Notice the distinction between deprotonation, the loss of H^+, which is what we see in the reaction

$$HOCl + H_2O \rightarrow OCl^- + H_3O^+$$

and the loss of complete hydrogen atoms, which is what has happened to the cysteines. To analyze the reaction in terms of the gain and loss of electrons we see that in cysteine the sulfur atoms were able to take more than their fair share of electrons from the relatively generous hydrogen atoms to which they were covalently bound. However, in the symmetrical disulfide bridge the electrons are equally shared, so each sulfur has lost electrons in the reaction with OCl^-.

Application of chlorine bleach causes the proteins of the extracellular aspect of cells and viruses to form disulfide bonds with each other, sticking them together and preventing their normal function. This is one of the many ways that chlorine bleach kills cells and deactivates viruses. The hypothesis that one action of chlorine bleach is to form disulfide bonds is from Winter et al. (2008) Cell 135(4): 691-701.

ANSWER: Calculate the fraction of hypochlorite that is protonated at pH 11.0

The pK_a of hypochlorous acid HOCl is 7.53. What percentage of the total hypochlorite is protonated at pH 11.0; that is, calculate the value of:

$$100 \times [HOCl] / ([HOCl] + [OCl^-])?$$

$pK_a = 7.53$ so $K_a = 10^{-7.53} = 2.95 \times 10^{-8}$

$$\text{but } K_a = \frac{[OCl^-]\ [H^+]}{[HOCl]}$$

$$\text{so } [HOCl]\ K_a = [OCl^-]\ [H^+]$$

let the total $[HOCl] + [OCl^-]$ be 100, so that we get the answer as a percentage, as required.

$$[HOCl]\ K_a = (100 - [HOCl])\ [H^+]$$

$$= 100\ [H^+] - [HOCl]\ [H^+]$$

$$\text{so } [HOCl]\ (K_a + [H^+]) = 100\ [H^+]$$

$$\text{so } [HOCl] = \frac{100\ [H^+]}{(K_a + [H^+])}\ \%$$

$$= \frac{100 \times 10^{-11}}{2.95 \times 10^{-8} + 10^{-11}}\ \%$$

$$= 0.03\ \%$$