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Kinetics and mechanisms of chlorine dioxide and chlorite oxidations of cysteine and glutathione

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Abstract

Chlorine dioxide oxidation of cysteine (CSH) is investigated under pseudo-first-order conditions (with excess CSH) in buffered aqueous solutions, p[H+] 2.7-9.5 at 25.0 degrees C. The rates of chlorine dioxide decay are first order in both ClO2 and CSH concentrations and increase rapidly as the pH increases. The proposed mechanism is an electron transfer from CS- to ClO2 (1.03 x 10(8) M(-1) s(-1)) with a subsequent rapid reaction of the CS* radical and a second ClO2 to form a cysteinyl-ClO2 adduct (CSOClO). This highly reactive adduct decays via two pathways. In acidic solutions, it hydrolyzes to give CSO(2)H (sulfinic acid) and HOCl, which in turn rapidly react to form CSO3H (cysteic acid) and Cl-. As the pH increases, the (CSOClO) adduct reacts with CS- by a second pathway to form cystine (CSSC) and chlorite ion (ClO2-). The reaction stoichiometry changes from 6 ClO2:5 CSH at low pH to 2 ClO2:10 CSH at high pH. The ClO2 oxidation of glutathione anion (GS-) is also rapid with a second-order rate constant of 1.40 x 10(8) M(-1) s(-1). The reaction of ClO2 with CSSC is 7 orders of magnitude slower than the corresponding reaction with cysteinyl anion (CS-) at pH 6.7. Chlorite ion reacts with CSH; however, at p[H+] 6.7, the observed rate of this reaction is slower than the ClO2/CSH reaction by 6 orders of magnitude. Chlorite ion oxidizes CSH while being reduced to HOCl, which in turn reacts rapidly with CSH to form Cl-. The reaction products are CSSC and CSO3H with a pH-dependent distribution similar to the ClO2/CSH system.

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