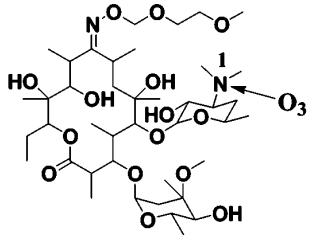
Water and wastewater treatment – Homework 8

1. pH-dependence of ozone reactions

Roxithromycin (RX) is a macrolide antibiotic, which can be oxidized at the tertiary amine moiety by ozone (see below). It has a pK_a of 9.2 and second order rate constants for the reaction with ozone of 1 $M^{-1}s^{-1}$ (protonated) and 10^7 $M^{-1}s^{-1}$ (deprotonated).



Roxithromycin (RX)

$pK_a = 9.2$

a) Sketch the pH-dependence of the apparent second order rate constant between pH 0 and 12.

b) What is the reactivity pK of RX?

c) What is the apparent second order rate constant for the oxidation of RX by ozone at pH 7? What is the half-life time for RX at pH 7 for a (constant) ozone concentration of 1 mg/L?

2. Oxidation of phenylurea herbicides

Some phenylurea herbicides have been oxidized in a drinking water treatment plant using ozone. The second-order rate constants for their reaction with ozone and OH radicals are given in the table below:

Pesticides	$k_{O3,P}$, $M^{-1}s^{-1}$	$t_{1/2}$ for only O_3	$k\bullet_{OH,P}$, $M^{-1}s^{-1}$
Isoproturon	141	250s	$5 \cdot 10^9$
Chlortoluron	51	11 min	$4 \cdot 10^9$
Diuron	15	40 min	$4.5 \cdot 10^9$

a) Formulate the rate equation for the oxidation with ozone and OH radicals.

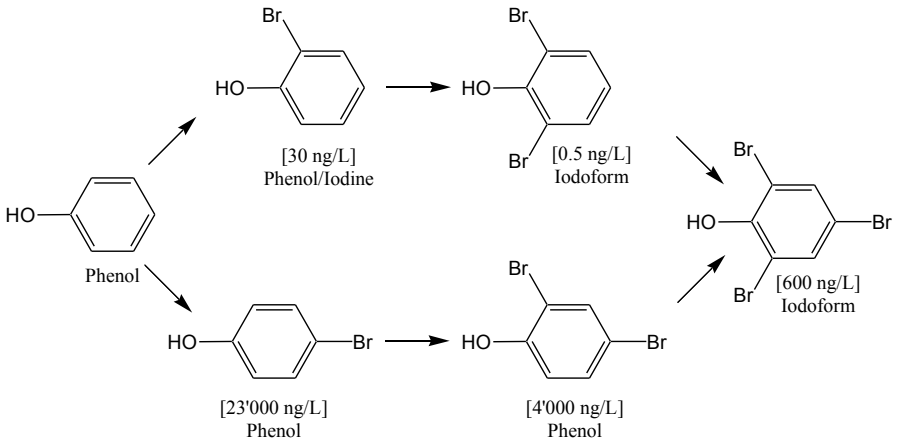
b) Assuming a reaction with ozone only, how can the half-lives given in the table be estimated? What was the corresponding ozone concentration (consider ozone concentration constant)?

c) In lake Zurich water a typical ratio R_{ct} (see lecture notes) of the concentrations of OH radicals and ozone is 10^{-8}. What is the fraction of each pesticide reacting with ozone and with OH radicals, respectively?

d) What is the degree of transformation for an ozone exposure of 0.015 M s?

3. Formation of bromophenols during chlorination

Bromophenols can be formed in bromide- and phenol containing waters. They are problematic in drinking water because of their low threshold for taste and odor. Bromophenols are formed by a bromination of phenol according to:



The values given in the brackets are the taste and odor threshold concentrations (reference taste below).

For the formation of bromophenols an oxidation of bromide is necessary prior to the bromination reaction. This reaction occurs according to:

$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad k = 1.5x10^3 M^{-1}s^{-1}$$

a) What is the half-life of bromide for a constant total HOCl concentration of $2x10^{-5}$ M (~ 1mg/L) at pH 6, 7 and 8 ($[HOCl]_{tot} = [HOCl]+[OCl^-]$, pKa(HOCl) ≈7.5)?
Hint: To calculate the half-life time of bromide, the speciation of HOCl has to be considered, because only HOCl reacts with bromide.

b) In a water containing ammonia, the reaction between HOCl and bromide may be suppressed if the concentration of ammonia is higher than the concentration of chlorine.
i) Formulate the corresponding reactions and a kinetic expression for the chlorine consumption.

ii) What is the fraction of HOCl reacting with bromide for a total chlorine concentration of $2x10^{-6}$ M, an ammonia concentration of $4x10^{-6}$ M and a bromide concentration of $2x10^{-7}$ M? Information: pH = 8, pK_a (NH_4^+) = 9.3, k(HOCl, NH_3) = $4.2x10^6 M^{-1}s^{-1}$.