Comment on "Oxidation of antibiotics during water treatment with potassium permanganate: Reaction pathways and deactivation [Hu et al., Environ. Sci. Technol., 2011, 45, 3635-3642]"

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In their article, Hu et al. [1] investigate the oxidation of three antibiotics (ciprofloxacin, lincomycin, and trimethoprim) by potassium permanganate. The authors propose detailed mechanistic pathways for the oxidation of these substrates, but apparently do not consider the acid/base behavior of the compounds under consideration, resulting in erroneous mechanistic interpretations throughout the manuscript. The pH dependent speciation of the antibiotics and their degradation intermediates affects interpretations regarding the most likely point(s) of oxidative attack(s). Thus, the speciation of all compounds affects all proposed reaction pathways. Hu et al. [1] conduct their studies in buffered solutions at pH 7. Consequently, any mechanistic interpretation must be for the expected speciations of all relevant compounds at this pH.

On p. 3639, the authors - in referring to Scheme 3 and the proposed mechanisms for trimethoprim (TMP) degradation - make the following statement: "Oxidation on the C4=C5 bond yields **V**a, and further hydrolysis of the amide group in **V**a yields the carboxylic products **VI** or **I**." Compound "**I**" in Scheme 3 does not appear to have a "carboxylic" group. Because of the general failure by these authors to consider the acid/base behavior of the starting materials and intermediates, the likely errors in all proposed mechanisms will not be detailed individually and in completeness. Rather, a representative example will be given instead. In Scheme 2, the authors propose a dehydrative mechanism (i.e., loss of water) to obtain compound **III** from "*Int. D*." At pH 7, the carboxylic acid group on "*Int. D*" would be effectively entirely ionized, meaning that a loss of water to yield the ring-closed product **III** is impossible. Consequently, this mechanism is invalid, and another mechanism must be active (or the reactants and products are not accurately given).

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References

[1] L. Hu, A. Stemig, K. Wammer, T. Strathmann, Oxidation of antibiotics during water treatment with potassium permanganate: Reaction pathways and deactivation, Environmental Science and Technology 45 (2011) 3635–3642.