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# Reduction of Isoxazoles including Sulfamethoxazole by Aqueous $Fe^{II}$–Tiron Complex: Impact of Structures

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**Abstract**

Isoxazole (ISX) is a key moiety in a number of antibiotics and pesticides such as sulfamethoxazole. Various ISXs were found to be reduced at different rates in aqueous solution containing $Fe^{II}$ and tiron (a catecholate ligand), and the reduction products were identified by time-of-flight mass spectrometry to be the ring-cleavage analogs. Three types of complexes were found to likely form between ISXs and $Fe^{II}$–tiron species: type I forms through 3-N and ring-O; type II forms through 5-N/O and ring-N; and type III forms through 6-O and ring-N. Calculation results indicate that electron transfer (either $1^{st}$ or $2^{nd}$), not protonation or N-O bond dissociation, is most likely the rate-limiting step. Because of the much lower free energies of the complexes formed after ring cleavage than before ring cleavage, the complexation should occur either after or during ring cleavage. The solvent kinetic isotope effects for the reduction of 3-amino-5-methylisoxazole (AMX) and 3,5-dimethylisoxazole (DMX) were determined to be 1.992±0.068 and 1.209±0.079, respectively, indicating that a proton is likely involved in the rate-limiting step for AMX but not for DMX. Electrochemical cell experiments demonstrated that the electron transfer can be significantly facilitated by type I and type II complexation with 1:2 $Fe^{II}$–tiron complex, but only to some extent with free $Fe^{II}$. This study provided a promising strategy to apply a highly effective and low cost reductant for the removal of emerging contaminants from anoxic environments.

*Keywords:* Reduction, Sulfamethoxazole, Isoxazole, Fe(II)-tiron, Complexation, Electron transfer