MASTER'S THESIS

A mechanistic study of the oxidation of Na[VO(O₂)₂(bpy)] by HOCl and its DNA-cleavage activity

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A Mechanistic Study of the Oxidation of $Na[VO(O_2)_2(bpy)]$ by HOCl and its DNA-Cleavage Activity

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Abstract

DNA-cleavage activity has recently been demonstrated in a variety of vanadium(V)-peroxo complexes when photo-irradiated at neutral pH. Singlet oxygen, which is capable of DNA-scission, was shown to be produced during the photolyses of these complexes. In this work, we investigated the DNA-cleavage activity resulting from the oxidation of selected vanadium(V)-peroxo complexes by hypochlorous acid and *N*-bromosuccinimide at neutral pH. Significant DNA-cleavage activities were found in the $Na[VO(O_2)_2(bpy)]$ and the $K[VO(O_2)(dipic)(H_2O)]$ complex. These activities were seen to be complex concentration- and incubation (reaction) time-dependent. Further investigation of the oxidation of these two complexes by hypochlorous acid and *N*-bromosuccinimide at neutral pH was therefore undertaken.

Spectrophotometric titrations revealed a complex-to-oxidant stoichiometric ratio of 1 : 2 for the diperoxo complex, $Na[VO(O_2)_2(bpy)]$, with both oxidants studied. But a complex-to-oxidant stoichiometric ratio of 1 : 1 was found for its monoperoxo counterpart, $K[VO(O_2)(dipic)(H_2O)]$. Detailed quantitative analysis of the product mixtures showed that metavanadate(V) anion, VO_3^-, and chloride anion were the principal products of the oxidation with hypochlorous acid. Singlet oxygen was also detected using *trans-*

methoxyvinylpyrene, a highly-selective singlet oxygen probe, by HPLC-fluorescence detection technique.

Detailed kinetic study of the oxidation of the $[VO(O_2)_2(bpy)]^-$ complex by hypochlorous acid in 0.5 M phosphate buffer at neutral pH was carried out. Global kinetic analysis suggested a model consisting of two consecutive irreversible elementary reactions with a non-steady-state intermediate for this reaction. A proposed mechanism based on this kinetic model as well as the results from our stoichiometric study and product analysis is given as follows:

$$HOCl + [VO(O_2)_2(bpy)]^- \xrightarrow{k_1} [V(O)_2(O_2)]^- + bpy + Cl^- + O_2 + H^+$$

$$HOCl + [V(O)_2(O_2)]^- \xrightarrow{k_2} VO_3^- + Cl^- + O_2 + H^+$$

where k_1 and k_2 were found to be 18.5 ± 1.68 $M^{-1}s^{-1}$ and 1.05 ± 0.118 $M^{-1}s^{-1}$, respectively. The observed invariance of k_1 and k_2 with respect to a 5-fold variation of the total ionic strength of the reaction medium suggests that HOCl, and not OCl^-, is the kinetically relevant oxidant species at neutral pH.

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