

Название публикации:

High Catalytic Activity of Vanadium Complexes in Alkane Oxidations with Hydrogen Peroxide: An Effect of 8-Hydroxyquinoline Derivatives as Noninnocent Ligands

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Аннотация:

Five monomeric oxovanadium(V) complexes $[\text{VO}(\text{OMe})(\text{N}^{\ominus}\text{O})_2]$ with the nitro or halogen substituted quinolin-8-olate ligands were synthesized and characterized using Fourier transform infrared, ^1H and ^{13}C NMR, high-resolution mass spectrometry-electrospray ionization as well as X-ray diffraction and UV-vis spectroscopy. These complexes exhibit high catalytic activity toward oxidation of inert alkanes to alkyl hydroperoxides by H_2O_2 in aqueous acetonitrile with the yield of oxygenate products up to 39% and turnover number 1780 for 1 h. The experimental kinetic study, the C_6D_{12} and $^{18}\text{O}_2$ labeled experiments, and density functional theory (DFT) calculations allowed to propose the reaction mechanism, which includes the formation of $\text{HO}\cdot$ radicals as active oxidizing species. The mechanism of the $\text{HO}\cdot$ formation appears to be different from those usually accepted for the Fenton or Fenton-like systems. The activation of H_2O_2 toward homolysis occurs upon simple coordination of hydrogen peroxide to the metal center of the catalyst molecule and does not require the change of the metal oxidation state and formation of the $\text{HOO}\cdot$ radical. Such an activation is associated with the redox-active nature of the quinolin-8-olate ligands. The experimentally determined activation energy for the oxidation of cyclohexane with complex $[\text{VO}(\text{OCH}_3)(5\text{-Cl-quin})_2]$ (quin = quinolin-8-olate) is 23 ± 3 kcal/mol correlating well with the estimate obtained from the DFT calculations.