

Название публикации:

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

Авторы:

Gryca, I [1] ; Czerwinska, K [1] ; Machura, B [1] ; Chrobok, A [2] ; Shul'pina, LS [3] ; Kuznetsov, ML [5] ; Nesterov, DS [5] ; Kozlov, YN [4,6] ; Pombeiro, AJL [5] ; Varyan, IA [6] ; Shul'pin, GB [4,6]

[1] Univ Silesia, Inst Chem, Dept Crystallog, 9th Szkolna St, PL-40006 Katowice, Poland

[2] Silesian Tech Univ, Dept Chem Organ Technol & Petrochem, Krzywoustego 4, PL-44100 Gliwice, Poland

[3] Russian Acad Sci, Nesmeyanov Inst Organoelement Cpds, Ulitsa Vavilova 28, Moscow 119991, Russia

[4] Russian Acad Sci, Semenov Inst Chem Phys, Ulitsa Kosygina, Dom 4, Moscow, Russia

[5] Univ Lisbon, Inst Super Tecn, Ctr Quim Estrutural, Ave Rovisco Pais, P-1049001 Lisbon, Portugal

[6] Plekhanov Russian Univ Econ, Stremyannyi Pereulok, Dom 36, Moscow 117997, Russia

Сведения об издании:

Inorganic chemistry

Том: 57 Выпуск: 4 Стр.: 1824-1839

DOI: 10.1021/acs.inorgchem.7b02684

Опубликовано: FEB 19 2018

Тип документа: Article

Аннотация:

Five monomeric oxovanadium(V) complexes [VO(OMe)((NO)-O-boolean AND)(2)] with the nitro or halogen substituted quinolin-8-olate ligands were synthesized and characterized using Fourier transform infrared, H-1 and C-13 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 H₂O₂ in aqueous acetonitrile with the yield of oxygenate products up to 39% and turnover number 1780 for 1 h. The experimental kinetic study, the C₆D₁₂ and O-18(2) labeled experiments, and density functional theory (DFT) calculations allowed to propose the reaction mechanism, which includes the formation of HO center dot radicals as active oxidizing species. The mechanism of the HO center dot formation appears to be different from those usually accepted for the Fenton or Fenton-like systems. The activation of H₂O₂ 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 HOO center dot 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 [VO(OCH₃)(5-Cl-quin)(2)] (quin = quinolin-8-olate) is 23 +/- 3 kcal/mol correlating well with the estimate obtained from the DFT calculations.

Ключевые слова:

O-2-h₂o₂-vanadium derivative-pyrazine-2-carboxylic acid; h₂o₂-vanadium complex-pyrazine-2-carboxylic acid; aerobic oxidation; pyrazine-2-carboxylic acid; coordination chemistry; molecular-structure; vanadate anion; hydrocarbon oxygenations; oxidovanadium complexes; pyrazinecarboxylic acid

