447b Density Functional Study of the Mechanism of the Catalytic Activity of a “Vanadate/Pca/H_2O_2” Reagent

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DFT calculations were used to verify the plausibility of the mechanism of hydrocarbon oxidation by a “vanadate/PCA/H_2O_2” catalyst proposed by Shul'pin et al. [Shul'pin, G. B.; Kozlov, Y. N.; Nizova, G. V.; Süss-Fink, G.; Stanislas, S.; Kitaygorodskiy, A.; Kulikova, V. S. J. Chem. Soc., Perkins Trans. 2, 2001, 1351] on the basis of experimental observations. The proposed model reproduces the major experimental observations. A vanadium complex with one pca and one H_2O_2 ligand is the precursor to the species responsible for HOO· generation. Predicted dependences of the oxidation rate on initial concentrations of PCA and H_2O_2 have characteristic maxima, whose shapes are determined by the equilibrium concentration of the active species. Conversion of the precursors occurs by migration of hydrogen from coordinated H_2O_2 to the oxygen of a pca ligand connected to the vanadium atom. It has been shown that the generation of HOO· radicals cannot occur via direct cleavage of a V-OOH bond. Instead, HOO· radicals are formed via a sequence of steps involving lower activation barriers. The new mechanism for free radical generation underestimates the observed rate of hexane oxidation by less than an order of magnitude. The activation energy measured experimentally (63-80 kJ/mol) agrees very well with the calculated values (67-81 kJ/mol).