

Reactivity trends of Fe phthalocyanines confined on graphite electrodes in terms of donor-acceptor intermolecular hardness: Linear versus volcano correlations

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In this work, we have studied the interaction between the hydrazine N_2H_4 molecule with several FeN_4 macrocyclic complexes (FePc's). In order to modulate the electron density located on the metal center using iron-phthalocyanine (FePc) as the reference, we used substituted iron-phthalocyanines with different types of substituents electron-donating groups such as iron-tetraamino-phthalocyanine ($4(NH_2)FePc$) and iron-octamethoxyphthalocyanine ($8(OCH_3)FePc$), and with electron-withdrawing groups such as iron-tetranitrophthalocyanine ($4(NO_2)FePc$) and iron-hexadecachlorophthalocyanine ($16(Cl)FePc$), respectively. We have found that the energy of interaction between hydrazine and the Fe center in the macrocycle increases as the electron-withdrawing power of the substituents increases. When rate constants instead of currents are compared in a semilog plot versus $\chi^{\ddagger}D-A$, a linear correlation is found where $\log k$ increases as the intermolecular hardness of the systems decreases. © 2014 Elsevier B.V. All rights reserved.