

Substituent effects on metallophthalocyanines adsorbed on graphite on their activity for the electrooxidation of hydrazine.

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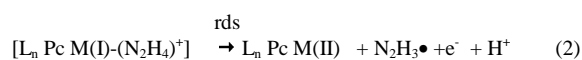
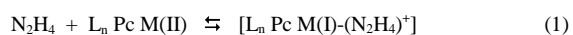
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In this work we have examined the effect of substituents on phthalocyanines of cobalt and iron on their catalytic activity for the electrooxidation of hydrazine. The activity of the different substituted phthalocyanines was examined by adsorbing them on graphite electrodes. The complexes used with electron-donating groups were: cobalt-octaethylhexyloxyphthalocyanine (CoOEHPc); cobalt-tetraneopentoxypthalocyanine (CoTNPPc); cobalt-tetramethoxyphthalocyanine (CoMeOPc); cobalt-tetraaminophthalocyanine (CoTAPc) and cobalt-2,3 naphthalocyanine (CoNPc). Unsubstituted cobalt-phthalocyanine (CoPc) was also used. Complexes with electron-withdrawing groups were cobalt-tetranitrophthalocyanine (CoTNPc) and cobalt-dodecafluorophthalocyanine (CoPcF₁₆).

Fig.1 shows typical results obtained for the oxidation of hydrazine catalyzed with cobalt phthalocyanines substituted with both electron-donating (left part of the curve) and electron-withdrawing (right part of the curve) groups on the periphery of the ligand. The data is presented as a plot of log I (at constant potential) versus Co(II)/(I) formal redox potential of the catalyst. For some complexes (on the right) the rate of the reaction increases with the driving force of the catalyst (measured as its redox potential) but for those on the left it decreases. The same plot is obtained when plotting log I versus the sum of the Hammett parameters of the substituents on the periphery of the phthalocyanine ring. A similar curve is obtained when the ligand is kept the same (phthalocyanine) and the metal is varied (Cr, Mn, Fe, Ni and Cu) and log I is plotted versus the number of d-electrons of the central metal.

Results similar to those in Fig.1 are obtained when using iron unsubstituted phthalocyanine (FePc) and substituted iron phthalocyanines with electron-donating groups iron-tetramethoxyphthalocyanine (FeMeOPc) iron-tetraaminophthalocyanine (FeTAPc) iron-tetracarboxyphthalocyanine (FeTCPc) iron-2,3 naphthalocyanine (FeNPc) and with electron-withdrawing groups were iron-tetranitrophthalocyanine (FeTNPc) and iron-dodecachlorophthalocyanine (FePcF₁₆).

The volcano-shaped curve in Fig.1 and that observed with Fe complexes (not shown) can be explained in terms of the early steps of the reaction (the overall reaction involves the transfer of 4-e⁻ to give N₂). According to the mechanism proposed below, the rate of the reaction will be given by $v = K_1 k_2 [L_n Pc M(II)][N_2H_4][OH^-]$. K_1 is the equilibrium constant of step 1 and k_2 is the rate constant of step 2. The chemical order of the reaction is one in hydrazine and in OH⁻ ions as found previously (1),



The maximum catalytic activity observed in Fig. 1 could be the result of a combined effect of steps 1 and 2 in the mechanism proposed above, that will affect the values of K_1 and k_2 . Electron-withdrawing groups will increase K_1 since they will stabilize the M(I) state. Electron-donating groups will favor step 2 (they stabilize the M(II) state) and increase the value of k_2 , which is the rate-determining step. The observed rate constant k is $K_1 k_2$ shows then a combined effect of both factors.

As indicated above, similar correlations to that shown in Fig.1 is obtained when the sum of the Hammett parameters of substituents is used instead of the redox potential. The concave downward volcano correlation of rates versus the sum of the Hammett parameters has been long known to be associated to effect where changing substituent changes the rate-determining step (2). This could be an alternative explanation as the catalysts on the ascending portion of the volcano exhibit Tafel slopes close to 0.12 V/decade whereas the complexes on the descending portion of the volcano show slopes close to 0.06V/decade. The mechanism presented in steps 1 and 2 agrees with a slope of 0.12 V. However, for complexes which formal potential in the region where the oxidation of hydrazine takes place, the surface coverage of M(II) species which are the active sites are potential dependent. This could decrease the Tafel slopes to 0.06V.

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Figure 1. Comparison of activities (as currents at constant potential) for the oxidation of hydrazine versus the formal potential of the Co(II)/(I) couple of different substituted cobalt phthalocyanines adsorbed on ordinary pyrolytic graphite. Data obtained at pH 13.

