

REACTIVITY METALLO-PHTHALOCYANINES ADSORBED ON GRAPHITE FOR THE ELECTROOXIDATION OF HYDRAZINE. CORRELATIONS WITH REDOX POTENTIALS HAMMETT PARAMETERS AND FRONTIER ORBITAL ENERGIES

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In this work we have examined the effect of the redox potential and Hammett parameters of substituent on the ligand of metallophthalocyanines on the catalytic activity of phthalocyanines for the electrooxidation of hydrazine. For this we use phthalocyanines of Cr, Mn, Fe, Co, Ni and Cu and also phthalocyanines of same metal (Co) with both electron-withdrawing and electron-donating substituents on the periphery of the phthalocyanine ligand, in order to modulate the Co(II)/Co(I) of the metal center. The activity of the different phthalocyanines was examined by adsorbing them on graphite electrodes. When comparing activities for the different metal chelates, a plot of $\log I$ (at constant potential) versus Co(II)/Co(I) redox potential a parabolic curve is obtained. For some complexes the rate of the reaction increases with the driving force of the catalyst (measured as its redox potential) but for most of them 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.

When comparing substituted cobalt phthalocyanines, those on the declining portion of the curve behave contrary to what is expected on thermodynamic grounds; *i.e.* the more oxidant phthalocyanines are the least active. A similar behavior has been observed for the electroreduction of oxygen and the electrooxidation of mercaptoethanol [1-3] and seems to be a common occurrence for inner-sphere reactions.

This could be explained in terms of the following scheme that includes the early steps of the reaction:



The effect of substituents L is probably reflected on step (2). Donor groups will favor this step (more negative redox potentials) increasing k . The opposite should be true for step (1). However, donor groups might also favor step 1 since they increase the electronic interaction between the HOMO of the donor (N_2H_4) and the LUMO of the acceptor (CoPc). We have checked this by carrying out both semi-empirical (PM3) and *ab-initio* (ROHF/CEP-31G) theoretical calculations of the energies of the frontier orbitals involved. This was used to estimate the intermolecular hardness η_{DA} of the different donor-acceptor pairs. The higher the hardness the lower the reactivity expected for step (3,4). Indeed, a plot of $\log k$ versus η_{DA} gives a linear plot where the rate of the

reaction decreases as η_{DA} increases. This provides an alternative explanation for the inverted correlation between $\log k$ and the Co(II)/Co(I) redox potential.

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