

The Catalytic Activities and Electron Configuration of Poly-Negative Phthalocyanine Complex Films with Lithium

Masaru ICHIKAWA, Mitsuyuki SOMA, Takaharu ONISHI and Kenzi TAMARU

Department of Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

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It was previously reported that various phthalocyanines exhibit marked heterogeneous catalytic activities in many reaction systems, such as the H_2 - D_2 exchange reaction, the hydrogenation of olefins, and the isomerization of butenes, at room temperature when they are exposed to a small amount of sodium or lithium.¹⁾

In this communication it will be demonstrated that such catalytic activities of the phthalocyanine electron donor-acceptor (EDA) complex films are not responsible for the reduced central metal ions of phthalocyanines, but for the poly-negatively-charged porphyrin ligands, where the excess electrons ($n=1$ to 4) are seemingly distributed in the π -systems.

Taube and other workers²⁾ have prepared many types of poly-negative ions of phthalocyanines, and their properties have been partly established by the iodine titration and measurements of the magnetic susceptibility of their stoichiometric salts with lithium.

In these experiments 50 mg portions of Fe-, Co-, Ni-, and Zn-phthalocyanines were reacted with lithium benzophenone ketyl, Li-naphthalene, Li, and Na in tetrahydrofuran at various stoichiometric ratios. The stoichiometric complex solutions exhibited their characteristic visible spectra. Various kinds of poly-negative ion complex films were prepared over silica wool (their surface areas were ca. 10 m²) by the evaporation of the solvent from each complex solution. The results of the iodine titration of the complex films were in agreement with the expected stoichiometry. The reactions were carried out in the temperature range between 20 and 120°C over each complex film in a closed circulating system (the dead-volume was ca. 140 ml). The reaction product was analyzed by gas chromatography using an alumina column. Some typical results are summarized in the table, as are the relative activities for the hydrogen-exchange reaction between molecular hydrogen and the hydrogen in each of the complex films, the H_2 - D_2 exchange reaction, the hydrogenation of propylene, and also the electron configuration of each poly-negative ion of the phthalocyanines,

TABLE

Complex	Electron configuration	D_2 -HZ ^{a)} 3 + log k	H_2 - D_2 ^{b)} 3 + log k	C_3H_6 + H_2 ^{c)} % conversion
FePc	d_6	—	—	—
LiFePc	d_7	—	—	—
Li_2 FePc	d_8	0.1	0.2	—
Li_3 FePc	$d_9 + \pi$	0.6	0.9	10
Li_4 FePc	$d_9 + \pi^2$	2.0	2.1	70
NiPc	d^8	—	—	—
LiNiPc	$d^8 + \pi$	0.4	0.3	5
Li_2 NiPc	$d^8 + \pi^2$	1.3	1.3	28
Li_3 NiPc	$d^8 + \pi^3$	1.7	2.0	60
Li_4 NiPc	$d^8 + \pi^4$	2.1	2.5	82

a) HZ represents the EDA complexes.

k (hr⁻¹) at 60°C, P_{D_2} = 12.5 cmHg

b) k (hr⁻¹) at 60°C, $P_{H_2+D_2}$ = 15 cmHg, $H_2:D_2$ = 1:1

c) $C_3H_6:H_2$ = 1:2 at 60°C in 20 hr.

which were reported by Taube.

It is suggested in this table that the catalytic activities for the hydrogen exchange and hydrogen chemisorption are not observed even at higher temperatures over the $FePc^{-1}$, $FePc^{-2}$, and $CoPc^{-1}$ complex films with lithium cations, in which one or two electrons are localized in their bivalent central metal ions. However, the H_2 - D_2 exchange reaction and the hydrogenation of propylene takes place at a considerable rate at room temperature over the $FePc^{-3}$, $FePc^{-4}$, $CoPc^{-2}$, ..., $CoPc^{-5}$, $NiPc^{-1}$, ..., $NiPc^{-4}$, and $ZnPc^{-1}$, $ZnPc^{-4}$ complex films, in which excess electrons are delocalized in the π -system of the porphyrin ligands. In addition to this, such complex films of higher negative ions as $NiPc^{-4}$ and $NiPc^{-3}$, $CoPc^{-5}$, and $FePc^{-4}$ are much more active for the reactions than the complex films of a lower negativity under similar reaction conditions. As the number of delocalized electrons in the porphyrin ligand increases, the reactivities of the porphyrin are markedly enhanced. Upon contact with hydrogen gas, the absorption peaks of $FePc^{-4}$ (620 and 860 m μ) gradually decrease and new peaks appear in the regions of 570 m μ and 520 m μ ; these peaks resemble those of $FePc^{-3}$ and $FePc^{-2}$. The spectra were restored completely to that of the $FePc^{-4}$ complex film by evacuation at 40°C for several hours.

1) M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, **63**, 1215 (1967).

2) R. Taube, *Z. Chem.*, **6**, 8 (1966); J. A. Elving and A. B. P. Lever, *J. Chem. Soc.*, **1961**, 1217; R. Taube and H. Munke, *Angew. Chem.*, **75**, 639 (1963).