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LETTERS TO THE EDITORS

Exchange Reaction of Hydrogen over the Electron Donor–Acceptor Complexes of Various Phthalocyanines with Sodium

The catalytic activity of phthalocyanines for the exchange reaction between hydrogen and deuterium at higher temperatures was first reported by Calvin, Cockbain, and Polanyi (*1*). The results, however, were not always reproducible (*2*). Acres and Eley recently studied the activation of hydrogen by poly (copper phthalocyanine) (*3*).

We have reported, in a previous paper (*4*), that the reactivity of phthalocyanines is strikingly affected by the addition of a small amount of electron donors by forming an electron donor–acceptor complexes, and that the hydrogen exchange between acetylene and the complexes takes place at room temperatures though pure phthalocyanines have no such reactivity even at 200°C. In this report the H_2–D_2 exchange over the electron donor–acceptor complexes of phthalocyanines with sodium has been studied.

Various phthalocyanines such as magnesium, iron, cobalt, and copper phthalocyanines were prepared by the ordinary method (*5*), and were purified by repeated sublimation and recrystallization from quinoline or α-chloronaphthalene. The composition of the isotopic mixture, H_2, D_2. and HD, was analyzed by means of gas chromatography (*6*).

Various phthalocyanines were sublimed on the surface of a glass vessel and a equimolar mixture of H_2 and D_2 was introduced to the pressure of 200 mm Hg. When only phthalocyanines were employed, no change was observed even at 200°C. However, it is of interest to note that various phthalocyanines which were exposed to sodium vapor exhibited marked activity for the exchange reaction between deuterium and hydrogen to produce hydrogen deuteride at room temperatures and that the deuterium content in the gas decreased, total hydrogen pressure staying constant. The decrease in the deuterium content suggests that the hydrogen atoms in the phthalocyanine molecules participate in the exchange reaction in the following manner: $D_2 + HZ = HD + DZ$, where HZ represents the phthalocyanines, and the decrease at equilibrium gives the number of the exchangeable hydrogen in HZ.

When acetylene was brought into contact with the phthalocyanine-Na complexes which had been deuterided by the contact with deuterium gas, deuteroacetylene was produced in the gas phase, which proves that the hydrogen of the complexes exchangeable with hydrogen can be replaced with those in acetylene.

The first-order rate constants for the H_2–D_2 exchange reaction over the phthalocyanines were in the following decreasing order: Fe, Mg, Co, and Cu phthalocyanines.

ESR measurements of the complexes revealed that the electron spin concentration increased by $10 \sim 10^3$ times through the addition of sodium vapor. It is accordingly concluded that the reactivity of phthalocyanines increased markedly by forming electron donor–acceptor complexes with sodium, and the hydrogen atoms in the complexes can exchange with molecular hydrogen, which is interesting in connection with the recent work on H_2–D_2 exchange reaction over tetracyanopyrene-cesium complex by Kondow, Inokuchi, and Wakayama (*7*).

Not only the exchange reactions, but also the hydrogenation and the isomerization reactions are being studied over these electron donor–acceptor complexes of phthalocyanines.

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The Role of Coordination Compounds in Poisoning of Heterogeneous Group VIII Reduced Metal Catalysts

Poisoning of metallic catalysts is a well documented but poorly understood phenomenon. It is generally considered to be a preferential adsorption effect dependent upon the formation of abnormally strong bonds between a catalyst and certain types of adsorbed species (*1*). While it is recognized that these bonds are of definite chemical type, neither the exact nature of the poison–metal interaction nor the chemical constitution of the adsorbed moiety has been defined. Empirical data indicate that formation of catalyst–poison bonds is limited to definite electronic structural features, namely, vacant *d* orbitals in the catalyst (*2*) and nonbonding electron pairs in the poison (*3*). These and similar observations coupled with the rapidly expanding knowledge of transition metal coordination chemistry have led to suggestions that there should be a strong correspondence between heterogeneous catalysis and the organometallic chemistry of the transition metals (*4*). However, direct evidence for the formation of specific coordination compounds on the surface of solid metal catalysts has not, as yet, been obtained. In this communication, we wish to report spectroscopic evidence that a specific type of coordination compound is formed on the surface of a silica-supported nickel catalyst when this catalyst is poisoned by H_2S while being used in the hydrogenation of an olefin.

Sulfur compounds are very effective poisons for reduced nickel and other Group VIII hydrogenation catalysts. However, toxicity is limited to compounds in which the sulfur possesses nonbonding electron pairs. These are believed to be involved in forming the strong chemisorptive bond with the catalyst, and, indeed, magnetic susceptibility data indicate, in the case of methyl sulfide poisoning, that the unshared electrons of the sulfur fill vacant *d* orbitals of the metal that otherwise would be available for catalysis (*5*). In view of the nickel sulfide–hydrogen equilibrium (*6*), the outstanding toxicity of sulfur, particularly at high temperatures and high partial pressure of hydrogen, cannot be explained on the basis of site-blocking or electronic changes