

conductors and their fundamental properties such as semi- and photo-conductivity and its temperature dependency have been elucidated.

In the field of catalysis many investigations have been made on the relation between the electronic properties of solid and its catalytic activity, and the theory of semi-conductor has successfully been applied to the problem of heterogeneous catalysis²⁾.

It is of interest to examine whether the organic semi-conductor would catalyze the exchange reaction between hydrogen and deuterium, as it would be a new type of catalytic reaction on a molecular crystal. It can also be noted on this problem that the ortho-para hydrogen conversion can be catalyzed by charcoal which is thought, from the X-ray diffraction analysis, to consist of many crystallites of graphitic carbon, in other words, large condensed polycyclic aromatic hydrocarbons.

The polycyclic aromatic compounds can react with bromine or iodine, the halogen atoms penetrating between the layers of the net planes. The halogen atoms thus chemisorbed might react with hydrogen to form hydrogen halide, the organic compound acting as a catalyst.

In order to obtain informations on these points the exchange reaction of hydrogen and deuterium in addition to the reaction between hydrogen and iodine has been studied in a static method in the presence of violanthrone, one of the organic semi-conductors.

The gas, H₂, HD and D₂, prepared from heavy water (47.5% D content) and sodium metal³⁾ was added to hydrogen to such an amount that the ratio of hydrogen deuteride to hydrogen was 0.326. The gas mixture was conducted to a reaction vessel at 18°C which contains 0.80 g. of violanthrone. The gas pressure was 307 mmHg. The reaction vessel was then heated up to 100° for 13 hours and a part of the gas mixture was taken out for mass spectrometric analysis, which showed no exchange reaction within the experimental error. From the statistical mechanical calculation, the activation energy for the exchange reaction could roughly be estimated as higher than 50 kcal. per mole.

Violanthrone (2.14 g.) was mixed with

Catalysis on an Organic Semi-Conductor

By Kenzi TAMARU and Takeo SHIMADA

(Received October 22, 1957)

Mostly because of the elaborate works of Akamatu and his co-workers¹⁾, it is generally recognized that the condensed polycyclic aromatic hydrocarbons and their related quinones are organic semi-

1) H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950); **20**, 1481 (1952); H. Inokuchi, *This Bulletin*, **29**, 131 (1956) etc.

2) K. Hauffe, *Advances in Catalysis*, Vol. VII, Academic Press, Inc., N. Y. p. 213 (1955).

3) A. Farkas and H. W. Melville, "Experimental Methods in Gas Reactions." Macmillan, London, 1939.

20.26 g. of iodine in a mortar, and 6.8 g. of the mixture was put in a reaction vessel, into which 402 mm. of hydrogen was introduced at 100°C. The reaction vessel was kept at 100° for nine hours, then at 130° for four hours and finally at 150° for four hours. No pressure change, however, could be observed other than that from the temperature change.

In short, the catalytic reaction neither between hydrogen and deuterium nor between hydrogen and iodine could be observed.

The assistance of Professor T. Titani and Professor S. Horibe of the Tokyo Metropolitan University in the mass spectrometric analysis is gratefully acknowledged. The authors are also indebted to Professor H. Akamatu of the University of Tokyo for his valuable suggestions and assistance.

*Department of Chemical Industry
Faculty of Engineering, Yokohama
National University, Minami-ku
Yokohama*
