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## NOTES

# Effect of Chemisorption of Hydrogen on Electrical Conductivity of Perylene-Cesium Charge-Transfer Complexes

Recently, we reported about the para–ortho hydrogen conversion reaction ($p\text{-}H_2 \rightleftharpoons o\text{-}H_2$) and the hydrogen–deuterium exchange reaction ($H_2 + D_2 \rightleftharpoons 2HD$) on aromatic-alkali metal charge-transfer complexes (*1*, *2*). Further, when deuterium gas was admitted onto these complexes, it was found that hydrogen exchange takes place between deuterium and the complexes (*3*).

Tamaru and his collaborators also studied the similar reaction on the phthalocyanine-sodium complexes and on some electron donor–acceptor complexes (*4*).

The kinetics of the parahydrogen conversion and of the $H_2$–$D_2$ exchange were studied as a function of temperature and it was found that the rate of reaction was first order at a constant pressure. On the basis of the temperature dependence of the rate constant, the activation energy, $E$ was estimated (*2*).

In this note, we will present the effect of hydrogen adsorption on the electrical conductivity of the complex.

The conductance cell used in this work was built up as follows: Vapor of cesium metal, prepared from a reaction between cesium chloride and calcium metal, was brought in contact with a thin film of perylene which had previously been deposited on the surface of a Pyrex glass plate with two aluminum electrodes *in vacuo*. By the contact between perylene and cesium vapor, an abrupt change in the color, from yellow to deep blue, occurred (*5*).* Figure 1 shows the schematic diagram of the cell.

The electrical resistivity of the complex, observed with the surface-type cell, was semiconductive in character ($\rho = \rho_0 \exp \epsilon/kT$), as Fig. 2 illustrates. The activation energy was 0.08 eV. The admission of purified hydrogen caused a remarkable rise in resistance, as Fig. 2 also illustrates. The effect was reversible, as on pumping out the hydrogen the resistance of the cell returned almost to its original value. Further, a series of measurements carried out over a range of temperatures (20–99°C) are plotted according to the $\log \rho$–$1/T$ relation in Fig. 2. As illustrated in the figure, the relation varied sublinearly below 60°C. These deviations may reflect the time lag of adsorption equilibrium of hydrogen on the complex. From the linear relation above 60°C, the estimated activation energy was 7 kcal/mole (0.3 eV). A similar phenomenon, the abrupt change of the conductivity, was found for the complex between tetracene and cesium, when hydrogen was admitted.

We have already reported that the hydrogen–deuterium exchange reaction ($H_2 + D_2 \rightleftharpoons 2HD$) takes place on the perylene-cesium charge-transfer complex in the temperature range from room temperature to 100°C and above 130°C the hydrogen

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* The formation of the charge-transfer complex was terminated by the saturation of the cesium metal involved.

exchange occurs between deuterium and the complex (*3*). On the basis of these results, the abrupt change of the electrical resistivity corresponds with the chemisorption of hydrogen onto the complex, but not with the exchange of hydrogen.

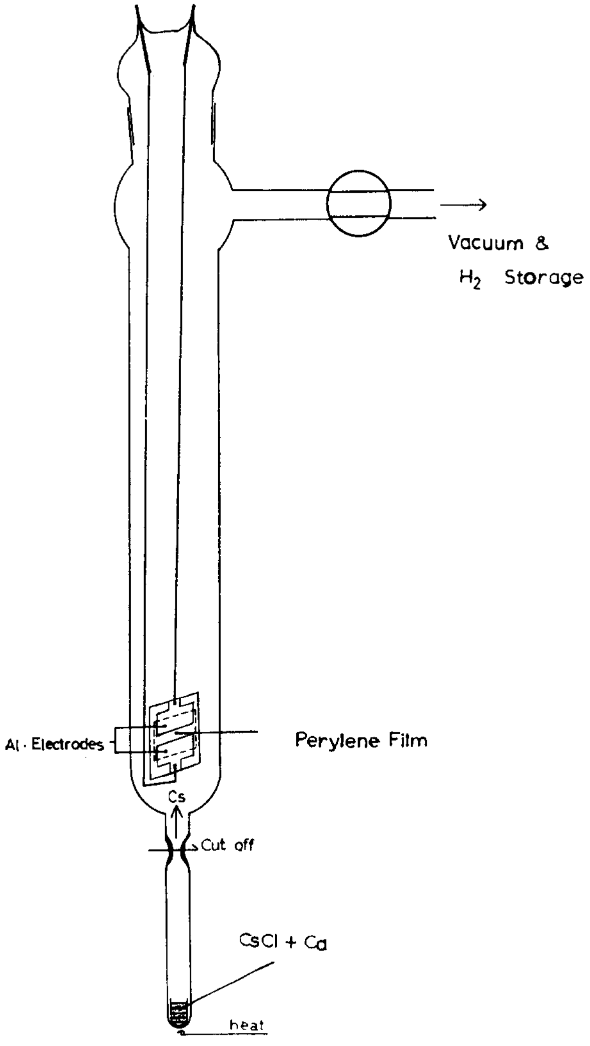

FIG. 1. The apparatus to investigate the resistance of the perylene-cesium complex film.

The temperature dependence of the electrical resistivity may be due to that of the number of hydrogen atoms formed on the surface in chemisorption.

It is very interesting that the activation energy for the conductivity, $\epsilon$, is similar to that ($E$) for the hydrogen–deuterium exchange reaction, viz. 6 kcal/mole (*6*).

Sachtler *et al.* have reported that the increase in resistance observed when molecular hydrogen is admitted to specially clean metal films is to be taken as evidence for the formation of covalently bound H, rather than $H^-$ ions (*7*). In the case of the organic free radical, $\alpha,\alpha'$-diphenyl-$\beta$-picrylhydrazyl, Eley and Inokuchi proposed the formation of a covalent link between the free radical and the hydrogen atoms diffused through the palladium electrodes (*8*).

In this work, we also expect the formation of some kind of a covalent link between the complex and hydrogen, the latter immobilizing the conduction electrons. This assumption is supported by the detection of NMR absorption of the graphite-cesium complex on which hydrogen is adsorbed (*9*).

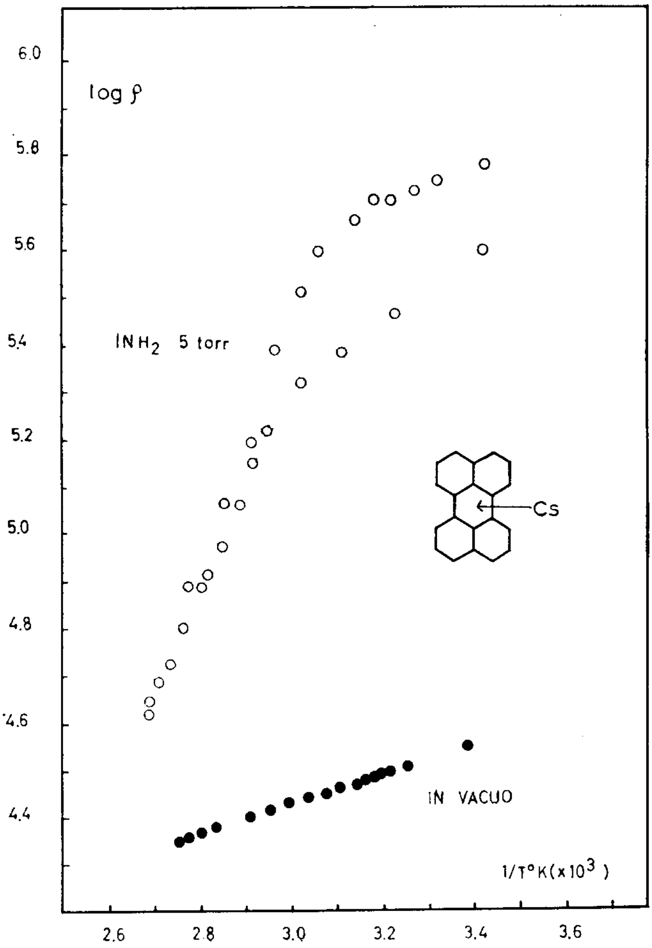

FIG. 2. The temperature dependence of the electrical resistivity of the complex *in vacuo* (full circles) and in 5 mm Hg of $H_2$ (open circles). The specific resistivity of the complex *in vacuo* is around $10^0$ Ω-cm at room temperature.

It is clear that these results indicate more definite information for the mechanism of chemisorption onto the charge-transfer complex.

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# Thermal Titration of Platinum Black and the Initial Heat of Adsorption for Hydrogen

Chon *et al.* (*1*) reported a method for preparing a platinum black surface by thermal titration of the adsorbed oxygen monolayer with gaseous hydrogen. In that paper and others (*2*, *3*, *4*), there are reported different values for the initial heat of adsorption for hydrogen and there are disagreements on the shape of the heat of adsorption curve at low coverage. In this note, data are reported which show that thermal titration does indeed provide a clean and reproducible surface and that the initial heat of adsorption of hydrogen on platinum black at 280°K is 17.5 ± 0.2 kcal/mole $H_2$.

These data were obtained using a calorimeter similar to that used by Greyson and Aston (*5*) except that the adiabatic shields and the heat exchanger were automatically controlled. The automatic shield controls allowed convenient observation of temperature changes of the sample for 8–10 hr and longer until temperature equilibrium was established. The system for handling and measuring the amount of gas introduced into the calorimeter was similar to that previously described (*6*). The volumetric and manometric equipment were calibrated.

Both hydrogen and oxygen gases used contained less than 10 ppm of impurities. These gases in addition were transferred to the glass supply bulbs from the high-pressure steel cylinder sources through liquid nitrogen cold traps. In the case of hydrogen the cold trap contained activated charcoal.

The platinum black, obtained from Engelhard Industries, Newark, N.J., was cleaned by initially outgassing at 470°K to a final pressure $<10^{-5}$ mm Hg, then titrating with hydrogen at 280°K. The water formed was removed from the sample by desorbing into a liquid helium cold trap and weighed. As the hydrogen added approached the amount of oxygen in the monolayer (calculated from BET surface area and crystallographic site density), the volume of the hydrogen increments was reduced and the water formed was removed after prolonged pumping by the cold trap. From the material balance, the excess hydrogen was removed as water by back-titrating with gaseous oxygen.

A small amount of helium ($<10^{-2}$ mm Hg) was introduced into the calorimeter to facilitate heat conduction within the sample and to minimize sintering from localized high temperatures. After cleaning the platinum black by the above process, two series of measurements were made with the surface of the platinum partially covered with known amounts of oxygen. In the first series, the oxygen coverage, $\theta_{\mathrm{PtO}}$, was 0.160 and in the second series $\theta_{\mathrm{PtO}}$ was 0.050 (designated ▲ and ■, respectively, in Fig. 1). Figure 1 should be interpreted as follows: the curve to the left side of center ordinate, $\theta = 0$ represents the reaction $H_2 + \mathrm{Pt{-}O}_{(ads)} \rightarrow \mathrm{Pt}(H_2O)_{ads}$ while the curve on the right side of center ordinate represents $H_2 + 2\mathrm{Pt} \rightarrow 2\mathrm{Pt{-}H}_{ads}$. In each series of measurements, the hydro-