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Hydrogen Exchange between Deuterium and Charge-Transfer Complexes

Recently, we found that one of the charge-transfer complexes of the type alkali metal–polycyclic aromatic compounds, catalyzes the para–ortho hydrogen conversion and also the hydrogen–deuterium exchange reaction, indicating that the hydrogen and the deuterium molecules are chemisorbed on the surface of solid organic charge-transfer complexes (*1*, *2*). Similar phenomena were found on the complexes between phthalocyanine and sodium (*3*).

Further, when deuterium gas was introduced onto the charge-transfer complexes, it was found that the hydrogen exchange takes place between deuterium and the complexes. Figure 1 shows the decay of the concentration of deuterium in the gas phase and also the increase of hydrogen deuteride and of hydrogen removed from the complex violanthrene B–Cs complex (H–ϕ) as a function of time.

For these exchange reactions, we introduce the following two schemes:

$$D_2 + H - \phi \rightleftharpoons HD + D - \phi$$
$$HD + H - \phi \rightleftharpoons H_2 + D - \phi$$

where D–ϕ is the deuterized complex. From Fig. 1, we can easily assume $D_2 + H\text{–}\phi \rightarrow HD + D\text{–}\phi$ is predominant at an initial state of this exchange reaction.

The decay of the deuterium concentration obeyed the first order law, $\ln D_t/D_0 = -kt$, where D_0 and D_t represent the gas phase at initial point and t minutes after contacts with the catalytic material. On the basis of the effect of temperature on the rate constant, $k \propto \exp(-E/kT)$, we could determine an apparent activation energy E as illustrated in Table 1.

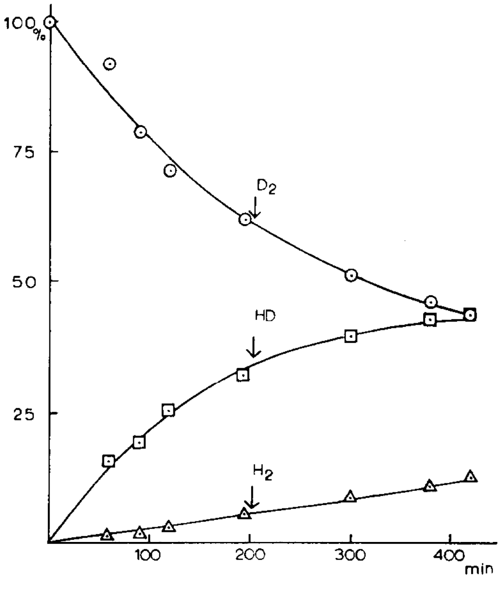
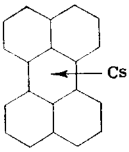
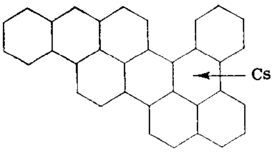


FIG. 1. The exchange reaction between deuterium and violanthrene B–Cs complex at 150°C.

To confirm the hydrogen–deuterium exchange reaction, the component of the charge-transfer complexes, the aromatic hydrocarbon, was analyzed by the method of mass spectroscopy. The deuterized complex (contact with D_2 for 7 hr at 150°C) was decomposed slowly with ethyl alcohol

TABLE 1
PERCENTAGES OF THE DEUTERIZED HYDROCARBONS IN THE CHARGE-TRANSFER COMPLEX

Complex	Deuterized hydrocarbon		E
Perylene-Cs	$C_{20}H_{11}D$	$C_{20}H_{10}D_2$ and others	—
	5%	2–4%	ca. 8–9 kcal/mole
Violanthrene B–Cs	All of deuterized violanthrene B		
	5–6%		17 kcal/mole

and then the aromatic hydrocarbon was isolated. From the result of mass spectroscopic analysis of the isolated hydrocarbon, we found that a part of the hydrogen of the hydrocarbon has definitely been exchanged with deuterium in a gaseous phase, as is shown in Table 1.

The concentration of deuterized aromatic hydrocarbon in the complex, however, was fairly low in comparison with the findings of the decay of D_2 concentration, mentioned in Fig. 1. This discrepancy may take place from the hydrogen exchange between the deuterized hydrocarbon and ethyl alcohol used for the decomposition of the complex.

This hydrogen exchange reaction occurs *reversibly*. This reversible behavior suggests that the complexes between certain aromatic compounds and alkali metal atoms may be similar to the model for hydrogenase, a biological enzyme (*4*).

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Effect of Sodium Ion Impurities in γ-Alumina on the Catalytic, Vapor-Phase Dehydration of Ethyl Alcohol

During studies of the kinetics of dehydration of ethyl alcohol vapor on alumina catalysts (*1*), we have examined how the activity and selectivity of highly pure γ-alumina (<100 ppm total impurities; Cu, Ni, Pb, Zn, Fe, and Mn) was affected by