JOURNAL OF CATALYSIS **11,** 143–146 (1968)

Catalytic Behavior of Organic Semiconductors

Hydrogen Exchange on Aromatic–Alkali Metal Charge-Transfer Complexes

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Received February 5, 1968; revised March 26, 1968

The hydrogen–deuterium exchange reaction ($H_2 + D_2 \rightleftharpoons 2HD$) was used to investigate the chemisorption of hydrogen $H_2 + D_2 \rightleftharpoons 2[H]_{ads} \rightleftharpoons 2[D]_{ads} \rightleftharpoons 2HD$; (I) on aromatic–alkali metal charge-transfer complexes, and also to examine the exchange between the gaseous deuterium and hydrogen of the complexes $D_2 + H\text{–}\phi \rightleftharpoons HD + D\text{–}\phi$; $HD + H\text{–}\phi \rightleftharpoons H_2 + D\text{–}\phi$; (II). Analyzing the reaction, the complexes may be classified into two groups, A and B: In the A group, the values of $[HD]^2/[HD_2]\,[D_2] = K$ for (II) always indicated thermodynamic equilibrium throughout the reaction; the K for the B group reached thermodynamic equilibrium after 2 or 3 months. Phthalonitrile-Na, naphthacene-Na, and tetranitropyrene-Cs belonged to the A group, and 1,3-dinitrobenzene-Na and tetranitropyrene-Cs, to the B group.

The values of the rate constant, k_{I}, for (I) have the following relationship: phthalonitrile-Na $\gtrsim$ naphthacene-Na $\gg$ 1,3-dinitrobenzene-Na. The k_{II} values for (II) have exactly the same relationship. A tentative explanation for such a large difference in reactivity can be based on the differences in interaction forces between the electron donor and acceptor in the solid phase.

INTRODUCTION

Since the hydrogen–deuterium exchange reaction was observed on the tetracyanopyrene-cesium complex (*1*), the catalytic activities of the charge-transfer complexes, typical organic semiconductors, have drawn much attention (*2,3*). In an earlier report (*2*), we have already described how the structure of the acceptor shows a strong selectivity for the catalytic activities; the hydrogen–deuterium exchange reaction for the tetracyanopyrene-Cs complex proceeds with a high velocity, but there is a very low velocity for the tetranitropyrene-Cs complex.

Further, we found that the hydrogen exchange reaction over the aromatic–alkali metal complexes occurs via two processes (*2*): by way of chemisorption onto the complexes;

$$H_2 + D_2 \rightleftharpoons 2[H]_{ads} + 2[D]_{ads} \rightleftharpoons 2HD \qquad \text{(I)}$$

and by way of exchange between the gaseous deuterium and hydrogen atoms of the complexes;

$$\left.\begin{aligned} D_2 + H - \phi &\rightleftharpoons HD + D - \phi \\ HD + H - \phi &\rightleftharpoons H_2 + D - \phi \end{aligned}\right\} \qquad \text{(II)}$$

The latter is denoted as $H_2 \rightleftharpoons D_2$ (*2*).* Since then, we have been studying the hydrogen exchange reaction on these complexes carefully in order to gain an insight into the mechanism of the reaction.

In this paper, we will present details of our measurement of the hydrogen–deuterium exchange processes over charge-transfer complexes, expecially the complexes between cyano- or nitro-substituted aromatic compounds and alkali metals. Further, we will

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* This abbreviation implies the exchange of hydrogen of the aromatic solid with deuterium in gaseous phase.

discuss the correlation between the reactivity of the complexes and their structures.

Experimental Procedure

The analysis of the hydrogen mixtures was carried out quantitatively by means of a gas chromatographic method, as has been described in the previous report (*2*). Phthalonitrile and 1,3-dinitrobenzene, obtained commercially, were recrystallized several times from their alcohol solutions and then purified by means of zone-refining. Naphthacene, tetranitropyrene (*4*), and tetracyanopyrene (*4*) were sublimed *in vacuo* several times in order to purify them. The charge-transfer complexes (50–100 mg) were prepared by bringing two components, organics and alkali metals, into direct contact in a Pyrex reaction vessel (about 100–150 ml) under a high vacuum. Deuterium was passed through a heated palladium thimble; a 1:1 mixture of normal hydrogen and deuterium at a pressure of 100 mm Hg was used.

Results and Discussion

Figure 1 shows the initial stage of the $H_2 \rightleftharpoons D_2$ reaction on the phthalonitrile-sodium complex. The situation for the complex between naphthacene and sodium* was completely comparable to that illustrated in Fig. 1.

On the other hand, the initial stage of the $H_2 \rightleftharpoons D_2$ exchange on the 1,3-dinitrobenzene-sodium complex was as is shown in Fig. 2. The reaction over the tetranitropyrene-sodium complex had a pattern similar to that of the 1,3-dinitrobenzene-Na complex.

The $H_2 + D_2 \rightleftharpoons 2HD$ reaction occurs via two paths, as has been mentioned above; one is the chemisorption (adsorption–desorption mechanism) of hydrogen on the complex [reaction (I)], while the other is the exchange between the gaseous deuterium and hydrogen of the complex [reaction (II), or $H_2 \rightleftharpoons D_2$]. Analyzing the curves in Figs. 1 and 2, we

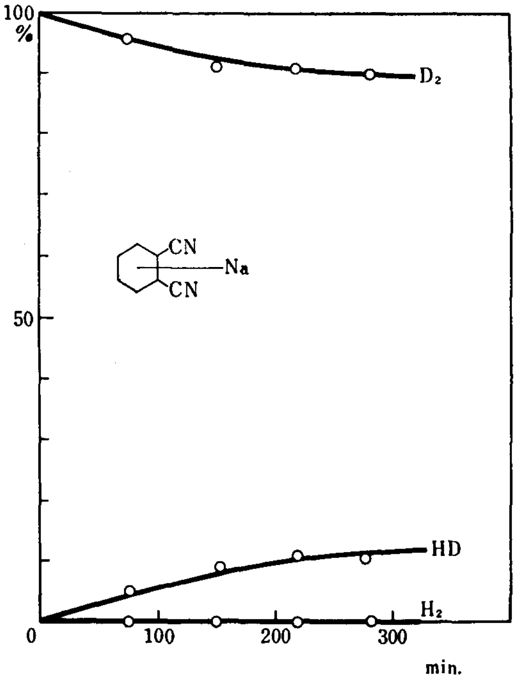

FIG. 1. The $H_2 \rightleftharpoons D_2$ reaction on the phthalonitrile-sodium complex at 95°C.

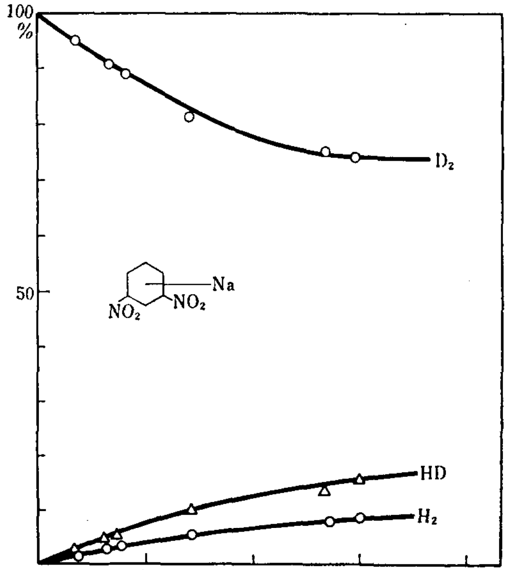

FIG. 2. The $H_2 \rightleftharpoons D_2$ exchange over the 1,3-dinitrobenzene-sodium complex at 120°C.

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* Detailed measurements of the hydrogen-deuterium exchange reaction have been carried out for two sorts of naphthacene-sodium complexes, naphthacene mononegative ion + Na^+ and naphthacene dinegative ion + $2Na^+$.

found that the value of $[HD]^2/[H_2][D_2] = K$ for $H_2 \rightleftharpoons D_2$ was always that of thermodynamic equilibrium throughout the reaction for the phthalonitrile-Na, tetracyanopyrene-Cs, and naphthacene-Na complexes, but not for the 1,3-dinitrobenzene-Na and tetranitropyrene-Na complexes, for which value of K reached a thermodynamic equilibrium after 2 or 3 months. The former group is denoted "A" and the latter "B" for convenience.

The experimental rate constant for the overall $H_2 + D_2 \rightleftharpoons 2HD$ reaction k, is given by

$$k = \frac{2.303}{t} \log \frac{C_0 - C_e}{C_t - C_e} \qquad (1)$$

where C_0, C_e, and C_t represent the concentrations of the deuterium at the initial point, in equilibrium, and after t minutes, respectively. When the rate constants for reactions (I) and (II) are described as $k_{\rm I}$ and $k_{\rm II}$, respectively, the overall rate constant k is written as

$$k = k_{\rm I} + k_{\rm II}$$

In reaction (II) the decay of the concentration of deuterium in the gas phase at an initial stage is described as

$$2.303 \log(D_t/D_0) = -k_{\rm II}t \qquad (2)$$

where D_0 and D_t represent the atomic concentrations of deuterium in a gaseous phase, at an initial point and after t minutes, respectively. The value of $k_{\rm II}$ can be estimated from Figs. 1 and 2.

For the A group, k was much faster than $k_{\rm II}$; then $k = k_{\rm I}$. However, $k \approx k_{\rm II}$ for the B group, thus $k_{\rm I} \approx 0$, as Table 1 shows. From these results, one can surmise that hydrogen is chemisorbed easily onto the surface of the A-group complex and that the equilibration occurs via the adsorption-desorption mechanism. Over the B group complexes, however, we assume that hardly any hydrogen is chemisorbed and that the hydrogen–deuterium exchange reaction occurs slowly via reaction (II) ($H_2 \rightleftharpoons D_2$).

These assumptions are supported by the results of the electrical conductivity measurement of the complexes (*5*); the admission of purified hydrogen to the naphthacene–alkali metal complex, of the A group caused a remarkable rise in the resistance, but no change in conductivity was found for the tetranitropyrene–alkali metal complex of the B group upon the admission of hydrogen.

What is the cause of these differences in

TABLE 1

THE RATE CONSTANT FOR HYDROGEN–DEUTERIUM EXCHANGE OVER THE COMPLEXES AT 95°C

Group	Complex		Rate constant[a]	
	Acceptor	Donor	$k_{\rm I}$	$k_{\rm II}$
A	Phthalonitrile	Na	10^4	10^2
	Naphthacene	Na	10^3–10^4	10^1–10^2
	Tetracyanopyrene	Cs	10^4	—[b]
B	1,3-Dinitrobenzene	Na	~0	1
	Tetranitropyrene	Na	~0	~1

[a] Relative value when $k_{\rm II}$ for 1,3-dinitrobenzene-Na complex is unity.

[b] Not observed.

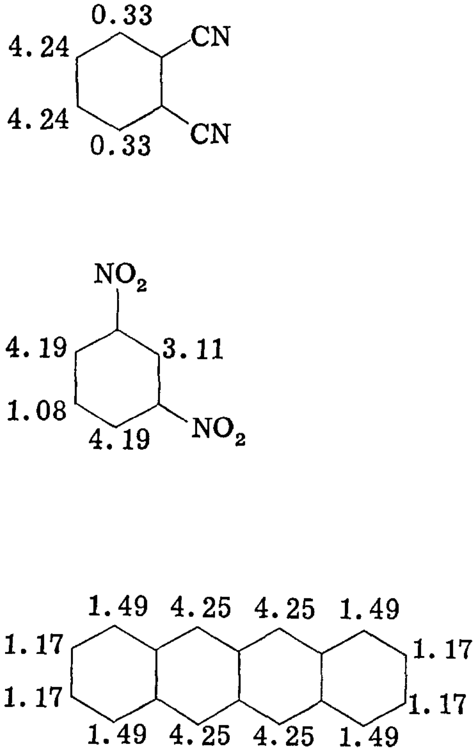

FIG. 3. The value ($a_{\rm H}$) of the proton splitting constants of the aromatic anion radicals.

the surface activity against the chemisorption? When we compare the values of the highest electron densities of the carbon atoms of the lowest vacant molecular orbital of neutral acceptors with the reactivity of their alkali metal complexes, no correlation can be found. The highest values of proton splitting constants (a_H) of phthalonitrile, 1,3-dinitrobenzene, and naphthacene negative ions are almost all equal, as Fig. 3 illustrates, but their complexes possess very different reactivities (see Table 1). For the complexes between alkali metal and tetracyano- and tetranitropyrene, the substituted groups of the acceptors strongly affect the reactivity of hydrogen–deuterium exchange rather than the elcetron densities on the carbon atoms of the polycyclic skeleton. A tentative explanation for such a large difference in reactivity between the A and B groups can be based on the differences in interaction force between the electron donor and acceptor in the solid phase. In the B group, the alkali metal reacts with the nitro group to make a strongly coupled ion pair, and then a "tight complex" is formed (*6*).* Figure 4 illustrates these assumptions.

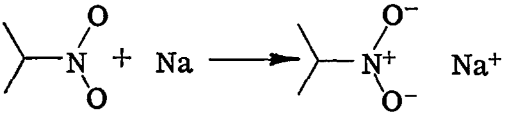

FIG. 4. The reaction between alkali metal and nitro group of aromatics.

Therefore, it is reasonable to assume that the residual reactivity over the complex with gaseous hydrogen is very weak. On the other hand, we can assume that the formation of the ion pairs of the A group is fairly loose; thus an excess charge on the aromatic anions in the solid-phase complex gives the reactivity with hydrogen, as has been described in the previous paper (*2*).*

The electrical conductivity of the cyano-substituted complex film is higher than that of nitro-substituted one, as Table 2 demonstrates (*4*). This result is consistent with that of ion-pair formation in the complex.

TABLE 2
THE SEMICONDUCTIVITY
[$\rho = \rho_0 \exp \Delta\epsilon/2k \times 288$ (°K)]
OF TETRACYANOPYRENE-Cs(1)
AND TETRANITROPYRENE-Cs(2)

	ρ (ohm-cm)	$\Delta\epsilon$ (eV)
(1)	6×10^6	0.70
(2)	2×10^5	0.94

ACKNOWLEDGMENTS

The authors wish to thank Dr. T. Kondow, Dr. Y. Mori, and Dr. M. Tsuda for their helpful discussion. One of us (N. W.) expresses his gratitude for receipt of a Scholarship of Tomonari Foundation.

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* This assumption is supported by the hydrogen–deuterium exchange reaction over trinitrobenzene–sodium complex, which will be reported elsewhere.

* The interaction between positively charged alkali metal and hydrogen in a solid has been studied by the calorimetric and nuclear magnetic reasonance methods (*7*).