

## Catalytic Behavior of Organic Semiconductors Hydrogen Exchange on Barium-Naphthacene Ion Salts

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The hydrogen exchange reaction on alkali metal- and alkali earth metal-naphthacene ion salts was observed by means of para-ortho hydrogen conversion. In the case of mononegative ion salt (naphthacene)<sup>-</sup>M<sup>+</sup>, the para-ortho hydrogen conversion proceeded by the physical mechanism. On the contrary, in the case of the naphthacene dinegative ion salts with alkali metal (naphthacene)<sup>2-</sup>2M<sup>+</sup>, the chemisorptive mechanism was predominant. Further, the hydrogen exchange over the (naphthacene)<sup>2-</sup>Ba<sup>2+</sup> salt occurred by way of exchange reaction between gaseous hydrogen and the hydrogen atom of the hydrocarbon. A proposal to explain the surface reaction is submitted.

Since we reported a catalytic behavior of tetracyanopyrene-cesium complex in (1965) (1), a number of studies concerning the catalytic activity of organic semiconductors have been published (2). In the previous works, we found two different mechanisms for chemical para-ortho hydrogen conversion on the aromatic-alkali metal ion salts (3)—a chemisorptive mechanism (Process I)\* and the exchange reaction between gaseous hydrogen and the hydrogen atom of the solid (Process II; H<sub>2</sub> ⇌ D<sub>2</sub>)\*.

It was shown that the reactivity depends strongly on the substitutional groups of aromatics, possibly due to the difference of the position of the positive ions (alkali metal ions) relative to the negative ions (aromatic ions) (4). Further, the contents of alkali metal were shown to affect strongly the reaction mechanism (5).

In the present study, an alkali earth metal, Ba, was used as a donor metal to give naphthacene anion salt and the para-

ortho hydrogen conversion and hydrogen-deuterium exchange reaction were studied on the naphthacene anion salts with various counter ions—Li<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, and Ba<sup>2+</sup>. Further, a model is proposed to explain the relation between the reaction mechanism and the ratio of the aromatic anions to the metal cations.

### EXPERIMENTAL PROCEDURES

The naphthacene-alkali metal ion salts were prepared as precipitates from their tetrahydrofuran solutions. The detailed description of the preparation method of the potassium salt was given in a previous paper (5).

The (naphthacene)-Cs<sup>+</sup> could be obtained in a similar way, where cesium metal is supplied by the reaction between cesium chloride and calcium metal *in vacuo*. However, since (naphthacene)<sup>2-</sup>2Cs<sup>+</sup> is hardly soluble in tetrahydrofuran, a filtration could not be used for separation of the complex and the residual cesium metal was carefully eliminated after naphthacene was completely reduced to dinegative ion.\*

\* The conversion by chemisorptive mechanism is denoted as Process I and the exchange by the reaction between gaseous hydrogen and the hydrogen atom of the ion salt is called Process II. The rate constants for these Processes, I and II, are denoted as  $k_I$  and  $k_{II}$ , respectively.

\* The detailed description of the preparation of the ion salt with Na or K has already been reported in Ref. (5). The preparation of the Cs-

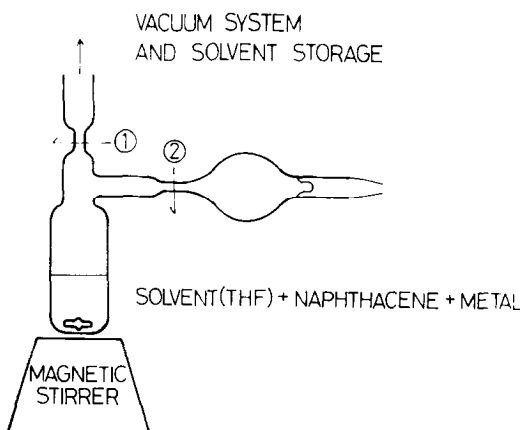


FIG. 1. The preparation of Ba(or Li)-naphthacene ion salt in tetrahydrofuran accompanying magnetic stirrer. When a lump of metal and naphthacene was introduced to the reaction glass vessel in advance, a water-free THF solvent was condensed into the vessel *in vacuo*. After sealing at point (1), the solution was stirred during 10 days to complete the formation of ion salt. The solution was transferred into a side glass cell and the ion salt prepared in the solution was dried-up onto the cell-surface by means of distillation of THF. Further, the cell was removed after sealing at point (2). The cell was connected to the reaction apparatus (3).

Because lithium and barium are not able to be distilled in the conventional glass apparatus, a lump of the respective metal was used to react with naphthacene dissolving in the tetrahydrofuran. To enhance the reaction velocity, a magnetic stirrer, as shown in Fig. 1, was applied. Stirring was continued for 10 days or more to complete the anion salt formation at room temperature.

salt carried out in a similar way; a completely degassed tetrahydrofuran (THF) was allowed to run into a reaction vessel, in which purified naphthacene and distilled cesium were stored in advance. After shaking the green [(naphthacene)<sup>-</sup>Cs<sup>+</sup>] colored THF solution was transferred into another vessel through a glass filter. The selection of the porosity of the glass filter was important to separate the residual cesium metal effectively from the matrix solution. The identification of the naphthacene ion was carried out by a spectroscopical method following Ref. (6). The shaking of the vessel was continued until the THF solution became blue [(naphthacene)<sup>2-</sup>2Cs<sup>+</sup>] to obtain dinegative ion. Since the dinegative ion salt was hardly soluble in THF, the salt suspended in THF was removed to another vessel by decantation.

The barium ion salt obtained in this way (precipitate of fine blue powder) was not soluble in tetrahydrofuran. Therefore, the residual lump of the barium metal was carefully eliminated (7).

The quantitative separation of the hydrogen mixtures—*p*-H<sub>2</sub> + *o*-H<sub>2</sub>, H<sub>2</sub> + D<sub>2</sub> or H<sub>2</sub> + D<sub>2</sub> + HD—was carried out by means of a gas chromatographic method, as described previously (3). The pressure of hydrogen in the reaction vessel was kept at about 100 mmHg and the volume of the reaction cell was about 120–150 ml.

## RESULTS

Table 1 summarizes the experimental results. In the case of mononegative ion salt, (naphthacene)<sup>-</sup>M<sup>+</sup>, *para*-*ortho* hydrogen conversion proceeded by the physical mechanism as described previously (5). Very slow chemical reaction was also observed, as was ascertained by the isotope exchange reaction. Here, the H<sub>2</sub> + D<sub>2</sub> ⇌ 2HD reaction proceeds at a rate comparable with that of H<sub>2</sub> ⇌ D<sub>2</sub> (isotope exchange reaction between gaseous deuterium and hydrogen atoms of the solid); Therefore, H<sub>2</sub> + D<sub>2</sub> ⇌ 2HD reaction is thought to occur predominantly by way of the later mechanism (Process II).

On the contrary, in the case of the naphthacene dinegative ion salts with alkali metal, *p*-H<sub>2</sub> ⇌ *o*-H<sub>2</sub> took place in parallel with the H<sub>2</sub> + D<sub>2</sub> ⇌ 2HD and the H<sub>2</sub> ⇌ D<sub>2</sub>

TABLE 1  
THE RATE CONSTANT (*k*) AND THE ACTIVATION ENERGY (*E*) OF *p*-H<sub>2</sub> ⇌ *o*-H<sub>2</sub> REACTION ON NAPHTHACENE ION SALTS

Ion salt	<i>k</i> (hr <sup>-1</sup> )	<i>E</i> (kcal/mole)
(Naphthacene) <sup>2-</sup> -Ba <sup>2+</sup>	2.7 <sup>a</sup>	2.7
(Naphthacene) <sup>2-</sup> -2Cs <sup>+</sup>	1.5 <sup>b</sup>	6.9
(Naphthacene) <sup>2-</sup> -2K <sup>+</sup>	3.8 × 10 <sup>-2</sup> <sup>b</sup>	7.8
(Naphthacene) <sup>2-</sup> -2Li <sup>+</sup>	5 × 10 <sup>-3</sup> <sup>b</sup>	6.7
(Naphthacene) <sup>-</sup> -Cs <sup>+</sup>	6 × 10 <sup>-2</sup> <sup>c</sup>	~0
(Naphthacene) <sup>-</sup> -K <sup>+</sup>	5 × 10 <sup>-3</sup> <sup>c</sup>	~0

<sup>a</sup> *k*<sub>II</sub>.

<sup>b</sup> *k*<sub>I</sub>.

<sup>c</sup> The rate constant of the paramagnetic conversion.

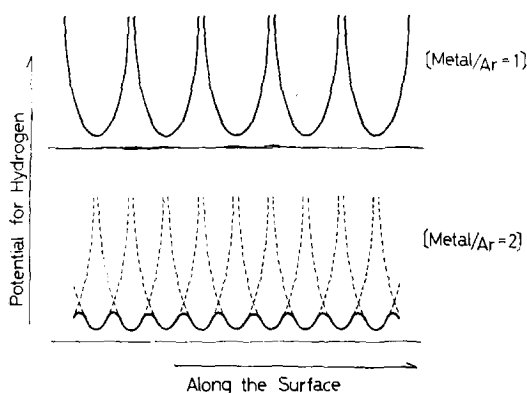


FIG. 2. A potential diagram for hydrogen over the aromatic-metal ion salt surface: (upper), the ratio of metal ion to the aromatic anion is unity, and (lower) the ratio is 2.

reaction at the initial stage is very slow. Therefore, on the dinegative ion salts the chemisorptive mechanism (Process I) prevails for the chemical conversion,  $H_2 + D_2 \rightleftharpoons 2HD$ .

A similar phenomenon was also observed on violanthrene A-sodium complex (5). In that study, it was shown that  $k_I/k_{II}$  (ratio of the rate of the chemisorptive reaction to that of the exchange reaction between the gaseous hydrogen and the hydrogen atom of the aromatic anion salt) falls with a decrease in the alkali-metal contents of the catalysts.

Considering these results, we propose that the potential for the hydrogen along the surface may be depicted as shown in Fig. 2. Here, the sites of the minimum potential correspond to the aromatic skeletons with the excess electron density (3), strongly attracted by the positive ions.

In the case of the low alkali-metal concentration, the adsorbed hydrogens are isolated from each other and the equilibration of the gaseous hydrogen can proceed by

way of the exchange between adsorbed molecules and the hydrogen atoms of the solid.

In the high alkali-metal concentration region, on the contrary, the chemisorbed hydrogens may be rather mobile and able to interact with each other to produce equilibrated mixtures of hydrogen over the surface as Fig. 2 illustrates.

The results of the reactivity of (naphthacene)<sup>2-</sup>Ba<sup>2+</sup> further support the above speculation: Because the ratio of barium ion to the aromatic anion is unity (both divalent species), the active sites on the ion salt are isolated. Then, it is easily understood that the  $H_2 + D_2 \rightleftharpoons 2HD$  reaction over the (naphthacene)<sup>2-</sup>Ba<sup>2+</sup> salt occurs preeminently by way of Process II. The distinguished reactivity may be due to the stronger Coulomb perturbation of the divalent positive ions to the aromatic anions.

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