JOURNAL OF CATALYSIS 14, 1–3 (1969)

# Catalytic Behavior of Organic Semiconductors

## Hydrogen Exchange on Aromatic–Alkali Metal Complexes as a Function of Donor Metals

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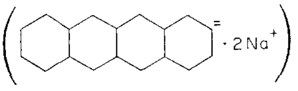
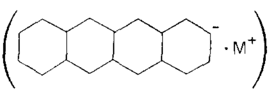
Received January 10, 1968; revised December 3, 1968

The catalytic activity of the complexes between the polycyclic aromatic hydrocarbons naphthacene (I), perylene (II), and violanthrene A (III) and the various alkali metals Li, Na, K, Rb, and Cs was observed by the rate and kinetics of the parahydrogen conversion, $H_2$–$D_2$ equilibration, and also of the $H_2$–$D_2$ exchange. The predominant mechanism for these complexes was found to be adsorption–desorption equilibration, the apparent activation energy ($E$) of the reaction for complexes (I) and (II) being independent of the type of donor alkali metals. However, $E$ for complex (III) decreased with increasing atomic number of the donors, Na < K < Rb < Cs. Further, the rate constants for these three complexes decreased in the order Li $\lesssim$ Na $\lesssim$ K < Rb < Cs. The cause of these differences in the surface activity may be understood qualitatively from the change of the ionization potentials of donor metals.

In the course of studies on the catalytic behavior of organic semiconductors (*1*, *2*, *3*) it was found that the content of alkali metal in the polycyclic aromatic hydrocarbon–alkali metal complexes strongly changes their catalytic activity (*4*): the naphthacene dinegative ion–sodium



or -potassium complex undergoes a strong chemical conversion, but for the mononegative ion–alkali metal



complex physical conversion is found as the predominant mechanism. Tamaru *et al.* have reported a number of studies closely related to this subject (*5*).

It is expected that the catalytic activity strongly depends on the sort of donor because of their difference in ionization potentials and ionic radii. In this paper, we present work on the catalytic activity of alkali metal–aromatic complexes as a function of the alkali metal donors.

Sodium and potassium, obtained commercially, were purified by a distillation procedure under vacuum to free them from hydrogen and carbohydrates. Rubidium and cesium were prepared from their chlorides by reduction with calcium metal in an evacuated glass tube: $2MCl + Ca \rightarrow 2M + CaCl_2$ (*1*). High-purity lithium, obtained commercially, was used to prepare its complexes with aromatic hydrocarbons from tetrahydrofuran solutions.

The conjugated aromatic hydrocarbons, naphthacene, perylene, and violanthrene A, purified chemically, were provided by J. Aoki and S. Iwashima. For further purification, these compounds were sublimed *in vacuo* repeatedly.

The preparation methods for the alkali metal–aromatic complexes employed in this experiment have already been described in the previous papers (*1*, *4*); one of them is a direct contact between alkali metal vapor and aromatic compound, thin film, or powder,* and the other is a precipitation from their tetrahydrofuran (THF) solutions.†

The catalytic activity of these complexes was observed by the rates and kinetics of the parahydrogen conversion, $H_2$–$D_2$ equilibration, and hydrogen–deuterium exchange. The quantitative analysis of the hydrogen mixture—p-$H_2$ + o-$H_2$, $H_2 + D_2$, or $H_2 + D_2 + HD$—was carried out by gas chromatographic methods, details of which have already been reported (*1*). The hydrogen pressure in the reaction vessel was kept at about 100 torr.

As mentioned in the previous paper (*3*) with regard to the exchange of adsorbed hydrogen over the complexes, there are two processes: (i) by way of chemisorption onto the complexes [$H_2 + D_2 \rightleftharpoons 2[H]_{ads} + 2[D]_{ads} \rightleftharpoons 2HD$; this reaction is denoted as reaction (I) and its rate constant by $k_I$] and (ii) by way of exchange between the gaseous deuterium and hydrogen atoms of the complexes [$D_2 + H - \phi \rightleftharpoons HD + D - \phi$ and also $HD + H - \phi \rightleftharpoons H_2 + D - \phi$; reaction (II) and its rate constant $k_{II}$]. From the analysis of the $H_2$–$D_2$ equilibration, it was found that the predominant process over the polycyclic aromatic–alkali metal complexes is reaction (I).

On the other hand, parahydrogen–orthohydrogen conversion took place in parallel with the $H_2 + D_2 \rightleftharpoons 2HD$ reaction; therefore the rate constant $k_I$ for chemisorption (adsorption–desorption mechanism) could be estimated from that of parahydrogen conversion.

TABLE 1

THE CATALYTIC ACTIVITY OF THE AROMATIC–ALKALI METAL COMPLEXES AS A FUNCTION OF DONOR METALS

| Alkali metal | $E$ (for $k_I$) (kcal/mole) | $k_I$ ($min^{-1}$) |
|---|---|---|
| | *Naphthacene–alkali metals* | |
| Li | 6.7 | + |
| Na | 7.8 | + |
| K | 7.8 | + |
| Cs | 6.9 | ++ |
| | *Perylene–alkali metals* | |
| Na | 6.6 | $6 \times 10^{-4}$ |
| K | 6.1 | $1 \times 10^{-2}$ |
| Rb | 6.0 | $2 \times 10^{-2}$ |
| Cs | 5.9 | $6 \times 10^{-2}$ |
| | *Violanthrene A–alkali metals* | |
| Na | 11.0 | $7 \times 10^{-5}$ |
| K | 7.2 | $6 \times 10^{-3}$ |
| Rb | 6.1 | $1 \times 10^{-2}$ |
| Cs | 3.0 | $6 \times 10^{-2}$ |

Table 1 shows the apparent activation energy $E$ of reaction (I) for the three types of complexes as a function of their donor metals. For naphthacene– and perylene–alkali metal complexes, the activation energy $E$ for reaction (I) is independent of the type of donor alkali metal, while the rate constants increase with the increase of their atomic numbers, Li $\lesssim$ Na $\lesssim$ K $\lesssim$ Rb < Cs. On the other hand, $E$ for reaction (I) of alkali metal complexes between Na, K, Rb, and Cs and violanthrene A decreases in this order and the order of magnitude for $k_I$ is the same as for the naphthacene and perylene complexes: Na $\lesssim$ K $\lesssim$ Rb < Cs.

What is the cause of these differences in the surface activity for different donor metals? The increase of the catalytic activity with the increasing atomic numbers of alkali metals may be understood qualitatively from the change of the ionization potential ($I$) of alkali metals: Li $I$ (gas) = 5.39 eV, work function = 2.4 eV; Na, 5.14 eV, 2.2 eV; K, 4.34 eV, 2.2 eV; Rb, 4.18 eV, 2.2 eV; and Cs, 3.89 eV, 1.9 eV. The amount of the excess charge on the aromatic anion, which seems to play an essential role in this catalytic activity (*4*), may increase with decrease of $I$ of the alkali metals. However, in order to find how the change of activation energy is related to the nature of the aromatic hydrocarbon the electronic and/or steric structures of the complexes have to be analyzed quantitatively.

We will extend our study by making

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* The violanthrene A–alkali metal and perylene–alkali metal complexes were prepared by the direct method. The complexes contained the maximum amounts of alkali metals; the mole ratio between violanthrene A–alkali metal and perylene–alkali metal reached 1/4–5 and 1/ ∼ 2, respectively.

† The dinegative naphthacene ion–alkali metal complexes were precipitated from their THF solutions. The identification of the anion was carried out by a spectroscopic method.

structural analysis of the complexes in order to gain an insight into the reaction mechanism.

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