JOURNAL OF CATALYSIS 12, 15–18 (1968)

Catalytic Behavior of Organic Semiconductors

Relation between Reactivity and Valency of Aromatic Anion in Aromatic–Alkali Metal Complexes

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Received April 18, 1968; revised July 8, 1968

The content of alkali metal in the polycyclic aromatic hydrocarbon–alkali metal charge-transfer complex strongly affects the catalytic activity. The naphthacene dinegative ion–sodium or –potassium complex, $(\text{naphthacene})^{2-}2\text{Na}^+$ or $(\text{naphthacene})^{2-}2\text{K}^+$, possesses a strong chemical conversion and its activation energy is about 7.8 kcal/mole. As for the naphthacene mononegative ion–K complex, $(\text{naphthacene})^{-}\text{K}^+$, the rate constant for $p\text{-H}_2 \rightleftarrows o\text{-H}_2$ conversion shows scarcely any dependence on temperature (60 to −196°C), which suggests that the physical conversion on paramagnetic anion prevails. Similar phenomena are found for the violanthrene A–Na charge-transfer complex.

Catalysis of parahydrogen conversion and hydrogen–deuterium exchange reactions by charge-transfer complexes has been found to be remarkably efficient (*1*, *2*, *3*). Recently, we discussed the correlation between the reactivity of the complexes and their structures (*4*). However, because of the complexity of the reaction mechanism, there still remains some ambiguity.

In this paper, we will present the dependence of the catalytic activity against the contents of alkali metals in the charge-transfer complexes.

EXPERIMENTAL PROCEDURES

The preparations of the charge-transfer complexes used in this experiment were carried out by two methods. First, sodium vapor was brought into contact with a deposited film of violanthrene A* on a glass vessel or the powdered sample. Completion of the complex formation was accelerated by heat treatment at 80–100°C for a few days. Details of the preparation apparatus have been reported in a previous paper (*5*).

Second, the naphthacene–alkali metal complexes were prepared as precipitates from their tetrahydrofuran solutions. Since negative ions of hydrocarbons are reactive towards oxygen and moisture, tetrahydrofuran (THF) had to be degassed carefully by the method shown in Fig. 1.

The flask (I), containing THF and a small amount of lithium aluminum hydride (LiAlH_4), was frozen by dipping in liquid nitrogen and pumped free of air. Then, THF was transferred into the trap (II) by distillation. This was repeated a few times to obtain completely degassed THF.

On the other hand, the fusion of alkali metal, put into a side glass tube, was accomplished by the application of a soft flame, so that the metal ran into III″, leaving the dross behind. III‴ was then removed at the seal-off. After repeating these processes (III‴ → III″ → III′), the purified sodium was further distilled into the reaction vessel (III), in which naphthacene (50 mg) had been stored in advance.

When the degassed THF was allowed to

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* Violanthrene A ($C_{34}H_{18}$), carefully purified by chemical methods, was provided by J. Aoki. This was sublimed *in vacuo* repeatedly.

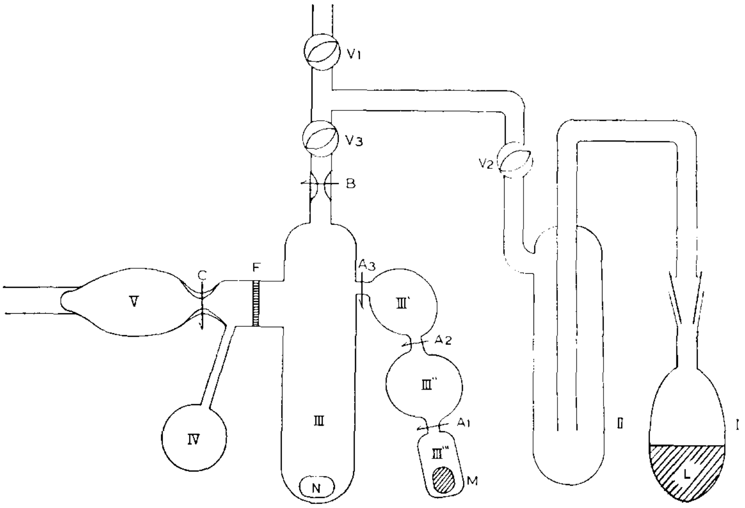

FIG. 1. Apparatus for the preparation of naphthacene–alkali metal charge-transfer complexes from their tetrahydrofuran solutions. L; Tetrahydrofuran, N, naphthacene and M; alkali metal.

run into the vessel III, a reaction between alkali metal and naphthacene occurred. The formation of mononegative naphthacene ion was detected by the change of color of the THF solution from orange to green.

When by shaking the neutral hydrocarbon was almost consumed to form the complex, the green THF solution was transferred into vessel (V; 120–150 cc) and optical cell (IV) through glass filter F. The cell (IV) was used to ascertain the identity of the reacted species by the spectroscopic method: Figure 2 shows the absorption spectra of mononegative naphthacene ion in THF solution. Finally, the THF solvent in (V) was distilled to (III) again and the vessel (V) removed at the seal-off C. Then, the reaction vessel (V) was connected to a high-vacuum line and was evacuated completely after breaking a seal.

To obtain dinegative ion, shaking of the vessel (III) was continued until the THF

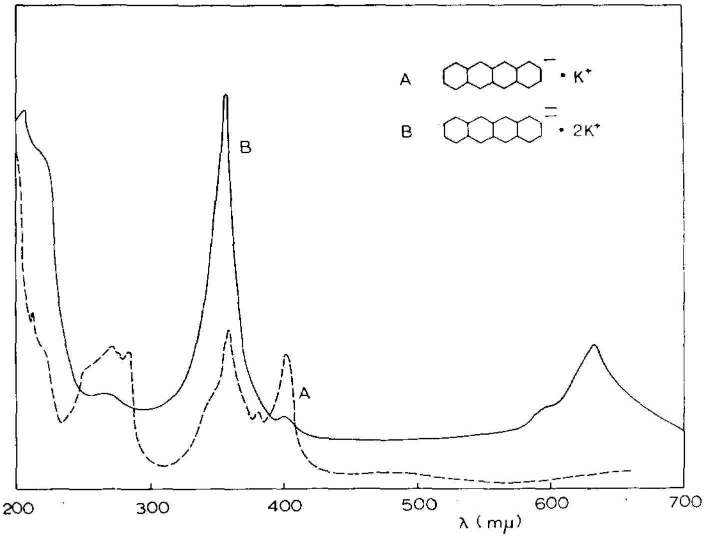

FIG. 2. The absorption spectra of mononegative and dinegative naphthacene ions in their alkali metal complexes.

solution became blue. In this case, the filter F should be more coarse than that used for preparation of mononegative species. The absorption spectrum of dinegative naphthacene ion is also shown in Fig. 2. These patterns agreed with those reported by Hoijtink and Zandstra (*6*).

The rates and kinetics of the parahydrogen conversion, H_2–D_2 equilibration, and also of hydrogen–deuterium exchange were applied to analyze their catalytic activites. The quantitative separation of the hydrogen mixtures — p-H_2 + o-H_2, $H_2 + D_2$, or $H_2 + D_2$ + HD—was carried out by means of a gas chromatographic method, as described in the previous report (*5*). The pressure of hydrogen in the reaction vessel was kept at about 100 mm Hg.

TABLE 1

The Dependence of Catalytic Activity of the Violanthrene A (VEA)–Na Complex against Na Contents (at 156°C)

	Na concentration in VEA (100 mg)–Na	k_I (hr^{-1})	k_{II} (hr^{-1})	k_I/k_{II}	Form
1	High[a]	5×10^{-3}	5×10^{-4}	10	Powder
2	High[a]	6×10^{-2}	6×10^{-3}	10	Film
3	Low	$\sim 10^{-2}$	3×10^{-2}	~ 1	Film
4	Very low	$\sim 10^{-5}$	1×10^{-4}	10^{-1}–1	Film

[a] Excess sodium metal remains on the surface of reaction glass vessel.

Results and Discussion

With regards to the exchange of adsorbed hydrogen over the violanthrene A–sodium complex, there are two processes at issue (*4, 7*); by way of chemisorption onto the complexes

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

[reaction (I), the rate constant k_I] and by way of exchange between the gaseous deuterium and hydrogen atoms of the complexes

$$\begin{matrix} D_2 + H - \phi \rightleftharpoons HD + D - \phi \\ HD + H - \phi \rightleftharpoons H_2 + D - \phi \end{matrix} \qquad (II)$$

(the rate constant k_{II}). In the high-temperature region (20–160°C), p-$H_2 \rightleftharpoons$ o-H_2 conversion took place in parallel with the $H_2 + D_2 \rightleftharpoons 2HD$ reaction. A similar relation was found for the reaction over naphthacene–alkali metal complexes prepared from their THF solutions. Therefore, the rate constant k_I for chemisorption (adsorption–desorption mechanism) could be estimated from that of parahydrogen conversion.*

The rate constant k_{II} was calculated from the decay of the concentration of deuterium in the gas phase at an initial stage (*7*). Table 1 shows the dependence of catalytic activity of the violanthrene A–sodium complex against alkali metal content; k_I/k_{II} falls with a decrease in alkali metal content of the complex.

The dependence on the content of donor metal was clarified definitely with use of naphthacene–Na and –K. In the case of dinegative ion complexes, (naphthacene)$^{2-}$2Na$^+$ or (naphthacene)$^{2-}$2K$^+$, the chemical mechanism of conversion proceeded strongly in the temperature range of 20–100°C as Table 2 shows, but at liquid nitrogen temperature the conversion hardly occurred. The activation energy of the chemical conversion was about 7.8 kcal/mole for both (naphthacene)$^{2-}$2Na$^+$ and (naphthacene)$^{2-}$2K$^+$.

As for the mononegative ion complex, (naphthacene)$^-$K$^+$, the rate constant showed scarce dependence on temperature (60° to −196°C), which suggests that the physical conversion on paramagnetic anions prevails (see Table 2).

In violanthrene A–Na complex, the maximum valency of the negative ion reaches four or five (*8*). A large variety in k_I/k_{II} for

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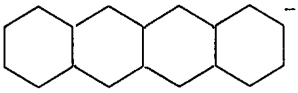
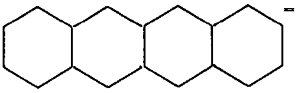
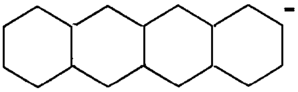
* The separation of the rate constants, k_I and k_{II}, for the hydrogen–deuterium exchange reaction has been reported in the previous paper (*4*).

TABLE 2

THE RATE CONSTANT k_I FOR HYDROGEN CONVERSION AND ITS ACTIVATION ENERGY FOR NAPHTHACENE–ALKALI METAL COMPLEXES

Complex	k_I (at 60°C) hr^{-1}	Activation energy kcal/mole
 (K^+)	5×10^{-3}	~ 0
 $2(K^+)$	2×10^{-1}	7.8
 $2(Na^+)$	2×10^{-1}	7.8

the complex may result from its multiple valencies.

On the specimens with a low concentration of alkali metal, 3 and 4 in Table 1, the adsorbed hydrogen appears to react more easily with the hydrogens of the aromatic molecule themselves than with the other adsorbed hydrogens ($k_{II} > k_I$), because the adsorption sites are localized.

The results support the view that excess charge on the aromatic anion gives a predominant mechanism (*5*), rather independent of the cation.

As an extreme case of the alkali metal–polycyclic aromatics charge-transfer complexes, several alkali metal–graphite lamellar compounds were prepared qualitatively with different ratios. These lamellar compounds, especially the C_8K compound, catalyze very strongly the hydrogen–deuterium exchange reaction (*5, 9*).

We now intend to make further studies on these substances including the hydrogen–deuterium exchange reaction, in order to gain an insight into the mechanism of the reaction.

ACKNOWLEDGMENTS

The authors wish to thank Dr. T. Kondow and Dr. M. Tsuda for their helpful discussion and one of us (N.W.) expresses his gratitude for financial support from the Tomonari Foundation.

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