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The Mechanism of the Reaction between Molecular Hydrogen and the Electron Donor-Acceptor Complexes (1:1 and 1:2) of Various Aromatic Hydrocarbons with Sodium[*1]

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The mechanism of the reaction between molecular hydrogen and the electron donor-acceptor complexes (A^-Na^+ and $A^{=}2Na^+$) of various aromatic hydrocarbons (A) with sodium were studied kinetically and spectroscopically. The relative activity of each electron donor-acceptor (EDA) complex for the hydrogen uptake was associated with its electronic properties, especially with the reduction potential of its anion. It was found that the hydrogen molecule reacts more readily with stronger electron-donating EDA complexes, whose anions have higher reduction potentials. It was also suggested that, on the hydrogen adsorption over the A^-Na^+ and $A^{=}2Na^+$ films (or in their solutions), the corresponding monohydroanion complexes (AH^-Na^+) and NaH were produced as follows:

$$2A^-Na^+ + H_2 = AH^-Na^+NaH + A$$
$$A^{=}2Na^+ + H_2 = AH^-Na^+ + NaH$$

The behavior of AH^-Na^+ was closely correlated with the localization energies of electrons in the anions of the aromatic hydrocarbons.

As has been demonstrated in previous papers, some catalytic reactions, such as the hydrogen exchange reaction of molecular hydrogen[1a)] (or acetylene[1b)]), the selective hydrogenation of unsaturated hydrocarbons[1c)], and the isomerization of butenes[1d)], take place readily at room temperature over the electron donor-acceptor (EDA) complexes of some aromatic compounds with strong donors, such as alkali metals, metallocenes, and phenothiazine.

The results obtained by electronic spectroscopy and ESR measurements suggest[2)] that these EDA complexes studied are, in general, characterized by having their ionic salt between the anion radical or poly-valent anions of aromatic compounds (A) and the cation radical or cations of donor atoms or molecules (D), which are formed by the charge-transfer as follows:

$$mA + nD = mA^{n-} + nD^{m+} \qquad (1)$$
$$n, m = 1 - 4.$$

In the solid state of the EDA complexes, their ion pairs come close to each other, resulting in strong electrostatic interactions.

Such stoichiometric EDA complexes are easily prepared, and various catalytic reactions proceed over their complex films[3a)] or in solutions, for instance, for the 1 : 1 and 1 : 2 anthracene-sodium complexes.[3b)]

In this investigation the stoichiometric EDA complexes of various aromatic hydrocarbons with sodium were prepared and the kinetics of the uptake of hydrogen was measured on their complex films and in their solutions. The behavior of the hydrogen

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[*1] A preliminary communication of this paper has been published in *J. Amer. Chem. Soc.*, **91**, 6050 (1969).

1) a) M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *J. Catal.*, **6**, 336 (1966); *Trans. Faraday Soc.*, **63**, 997, 1215, 2528 (1967); This Bulletin, **40**, 1015, 1294 (1967). b) M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *J. Phys. Chem.*, **70**, 2069, 3020 (1966), *Tetrahedron Lett.*, **47, 1966**, 5841, *Trans. Faraday Soc.*, **63**, 997, 1215 (1967). c) M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *J. Catal.*, **9**, 418 (1968); M. Sudo, M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *J. Phys. Chem.*, **73**, 1174 (1969); M. Ichikawa, M. Sudo, M. Soma, T. Onishi and K. Tamaru, *J. Amer. Chem. Soc.*, **91**, 1538 (1969). d) M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, **63**, 2012 (1967).

2) M. Szwarc, *Progr. Phys. Org. Chem.*, **6**, 323 (1968); R. Taube, *Z. Chem.*, **6**, 8 (1966); G. J. Hoijtink and P. J. Zandstra, *Mol. Phys.*, **3**, 371 (1960); P. H. Rieger, I. Bernal, W. H. Reinmuth and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **85**, 683 (1963); N. Hirota, *J. Amer. Chem. Soc.*, **90**, 3603 (1968).

3) a) M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, This Bulletin, **41**, 1739 (1968); *Z. Phys. Chem., N. F.*, **68**, 309 (1969); N. Wakayama and H. Inokuchi, *J. Catal.*, **11**, 143 (1968); **15**, 417 (1969); N. Wakayama, Y. Mori and H. Inokuchi, *J. Catal.*, **12**, 15 (1968). b) S. Tanaka, M. Ichikawa, S. Naito, M. Soma, T. Onishi and K. Tamaru, This Bulletin, **41**, 1739 (1968); M. Ichikawa, S. Tanaka, S. Naito, M. Soma, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, in press.

absorbed by the EDA complexes was also studied by means of UV, NMR, and ESR spectrometries.

Experimental

The stoichiometric EDA (1 : 1 and 1 : 2) complexes of aromatic hydrocarbons with sodium were prepared in a manner similar to that described previously.[3a,3b) A dry tetrahydrofuran (THF) or dimethoxyethane (DME) was allowed to run into a reaction vessel, in which purified aromatic hydrocarbon (*ca.* 3×10^{-3} mol) and distilled sodium (in excess) had previously been placed. After the reaction vessel had then been shaken at room temperature for a long time, a deep-colored complex solution was obtained. The 1 : 1 complexes of anthracene, pyrene, perylene, tetracene, and 1,2-benzanthracene were prepared by controlling the reaction between each aromatic hydrocarbon and sodium. After the identification of their compositions by means of their electronic absorption spectra,2) the complex solutions were introduced into the reaction cell through a glass filter.*2 The reaction-cell was equipped with a closed circulating system (the dead space of the reaction system was *ca.* 170 m*l*). The complex films were deposited on the glass wall or on silica wool by evaporating the solvent.

The complex films were evacuated further for a day at 90°C prior to the experiments. The complexes of weaker acceptors, such as biphenyl and naphthalene, were partly decomposed into their components by evacuation at 90°C, but other complex films of aromatic hydrocarbons with sodium were comparatively stable at higher temperatures, such as 120°C.

The uptake of hydrogen over the complex films and in solutions was determined by PVT measurements at a constant pressure or a constant volume.

The properties of the EDA complexes which adsorbed hydrogen were studied by the UV (HITACHI-spectrophotometer (EPS-2)), esr- (Varian Associates epr spectrometer), and NMR- (100 MHz high-resolution nmr-spectrometer (JEOL-JNR-4H100)) techniques.

Similar experiments were carried out for their complex solutions in THF or DME by introducing hydrogen.

Results and Discussion

I. The Kinetics of Hydrogen Adsorption over A^-Na^+ and $A^=2Na^+$ Films of Various Aromatic Hydrocarbons with Sodium. When hydrogen (10—35 cmHg) was applied to such complex films as biphenyl, naphthalene, pyrene, and phenanthrene with sodium (1 : 1) in the temperature range between 20 and 90°C, a small amount of hydrogen was adsorbed readily in the initial stage of the adsorption; further adsorption then proceeded slowly for several days, as is shown in Fig. 1, where the kinetics of hydrogen adsorption over the phenanthrene$^-$Na$^+$ complex film is presented. At temperatures higher than 60°C, a small amount of neutral acceptor molecules was separated from each complex film of these 1 : 1 complexes with the progress of the hydrogen adsorption in a manner similar to the case with anthracene$^-$Na$^+$.4)

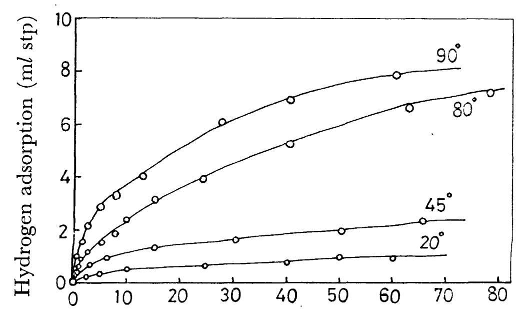

Fig. 1. The kinetics of the hydrogen adsorption over the phenanthrene$^-$Na$^+$ film (3×10^{-3} mol) at $P_{H_2}=20$ cmHg at the temperatures between 20 and 90°C.

The slow adsorption of hydrogen in the later stage continued at higher temperatures and reached the saturation point. Judging from the total amount of hydrogen adsorbed at the saturation point, it may be suggested that the hydrogen uptake took place homogeneously throughout the A^-Na^+ films.

The desorption of hydrogen was very slow, even at higher temperatures such as 90°C; the complexes were partly restored by evacuation at 100°C for 20 hr, and a trace of a neutral molecule was also separated from the reaction systems.

When the phenanthrene$^-$Na$^+$ (3×10^{-3} mol) was deposited over a silica gel,*3 the surface area of which was estimated to be 60 m^2 by the BET method using nitrogen, the hydrogen uptake at the initial stage for the same amount of the complex increased

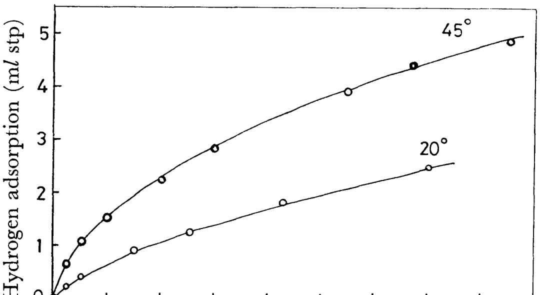

Fig. 2. The kinetics of the hydrogen adsorption on the THF solution of phenanthrene$^-$Na$^+$ (8×10^{-3} mol/50 m*l* of THF) at $P_{H_2}=20$ cmHg.

[*2] The separation of the residual sodium metal was achieved by taking special cape.

4) S. Tanaka, S. Naito, M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, **66**, 976 (1970).

[*3] The silica gel was evacuated at 400°C for 20 hr prior to use.

to several times that on the complex film deposited on the glass wall (the surface area was less than 1 m^2) under similar reaction conditions: $P_{H_2}=20$ cmHg, 65°C.

It was demonstrated that the uptake of hydrogen also occurred uniformly on a THF solution of the phenanthrene$^-$Na$^+$ complex, as is shown in Fig. 2, with simple first-order kinetics in the temperature range between 20 and 60°C.

It may, accordingly, be suggested that the slow adsorption in the later stage over the complex films is to be attributed to that hydrogen gas diffused with difficulty into the bulk from the surface of the complex films.

For the 1 : 2 complex films of anthracene,[4] pyrene, perylene, 1,2-benzanthracene, and tetracene with sodium, hydrogen was adsorbed at temperatures of 20 to 140°C with similar kinetics. Hydrogen was readily taken up in the initial stage, but thereafter was adsorbed rather slowly until saturation was reached. The hydrogen desorption from these 1 : 2 complex films took place slowly, but the complexes were restored completely by evacuation at 100°C for 20 hr without any appreciable decomposition of the complexes. It should be noted that only negligible amounts of the neutral molecules or other products were separated from these 1 : 2 complex films throughout the hydrogen adsorption.

The activation energies for the rate of the hydrogen uptake were measured over fresh 1 : 1 and 1 : 2 complex films of various aromatic hydrocarbons; the results are summarized in Table 1. The rates of hydrogen adsorption (V: m*l*/mol hr) listed were observed in the initial stage of the adsorption. The surface areas of all the complex films were found to be almost equal (less than 1 m^2) when the complexes were deposited on the glass wall of the vessel.

TABLE 1

Compelxes*	Amount of the complexes (mol)	V_{ads} (m*l*/mol hr) $P_{H_2}=20$ cmHg, 80°C	E** (kcal/mol)
Biphenyl$^-$Na$^+$	1.1×10^{-3}	1.8×10^2	10
Naphthalene$^-$Na$^+$	3×10^{-3}	3.2×10^2	10
Phenanthrene$^-$Na$^+$	3×10^{-3}	6.5×10^2	11
Anthracene$^-$Na$^+$	3.8×10^{-3}	1.0×10^2	15
Pyrene$^-$Na$^+$	4×10^{-3}	0.43×10^2	14
Anthracene$^=$2Na$^+$	5×10^{-3}	12×10^2	13
Pyrene$^=$2Na$^+$	4×10^{-3}	3.3×10^2	10
Perylene$^=$2Na$^+$	2×10^{-3}	0.38×10^2	14
Tetracene$^=$2Na$^+$	2×10^{-3}	0.14×10^2	17
Na	3×10^{-2}	negligible	—

* Each complex was deposited over the glass-wall of the reaction vessel (the surface area was less than 1 m^2). The complex formation was almost complete in a film at reaction conditions except the biphenyl$^-$Na$^+$, which exists less than 40%[2] of a given amount of biphenyl at an equilibruium in solution or in a film. The amount of the active biphenyl$^-$Na$^+$ complex was estimated from these consideration.

** The activation energies for the hydrogen adsorption were obtained from the Arrhenius' plots of the inititial rates of hydrogen adsorption (V_{ads}) at the temperatures between 20 and 90°C.

It was interesting to note that, for the 1:2 complex films of tetracene and perylene with sodium, only a trace of hydrogen adsorbed reversibly at temperatures from 20 to 90°C, and also that a slow adsorption (rather irreversible) occurred when the temperatures was raised above 110°C, as is shown in Fig. 3. The apparent activation energies of hydrogen uptake were estimated to be 14 and 17 kcal/mol over the perylene$^=$2Na$^+$ and tetracene-$^=$2Na$^+$ respectively.

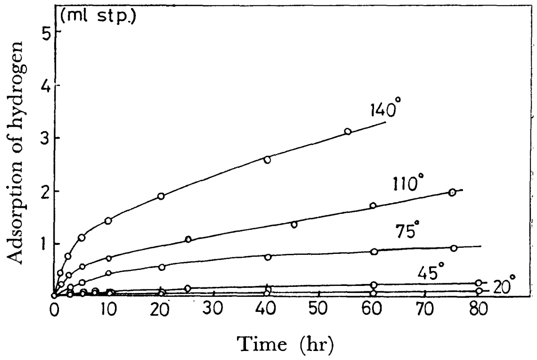

Fig. 3. The kinetics of hydrogen adsorption over the perylene$^-$2Na$^+$ film (1.0×10^{-3} mol, deposited on a silica gel (the surface area was *ca.* 46 m^2)) at $P_{H_2}=27$ cmHg. The dead volume of the reaction system was 168 m*l*.

II. Reactivities of Various EDA Complexes (A$^-$Na$^+$ and A$^=$2Na$^+$) for the Hydrogen Adsorption, and Their Electronic Properties. The rates of the hydrogen uptake were measured over the A$^-$Na$^+$ and A$^=$2Na$^+$ films (*ca.* 3×10^{-3} mol) of each of various aromatic hydrocarbons with sodium, which were deposited over silica gel (the surface area of which was *ca.* 60 m^2) by introducing hydrogen (26cmHg) at temperatures from 20 to 90°C. When the rates of hydrogen adsorption (V: m*l*/mol hr) were plotted against the reduction potentials of the mono- and di-anions of the corresponding aromatic hydrocarbons, a volcano-shape curve was obtained, as is shown in Fig. 4. Their reduction potentials ($-E'$ volt) have been obtained from the potentiometric measurements of Hoijtink and his coworkers'.[5]

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[5] J. Hoijtink, E. de Boer, P. H. van der Meij and W. P. Weijland, *Rec. Trav. Chim. Pays-Bas.*, **75**, 487 (1956).

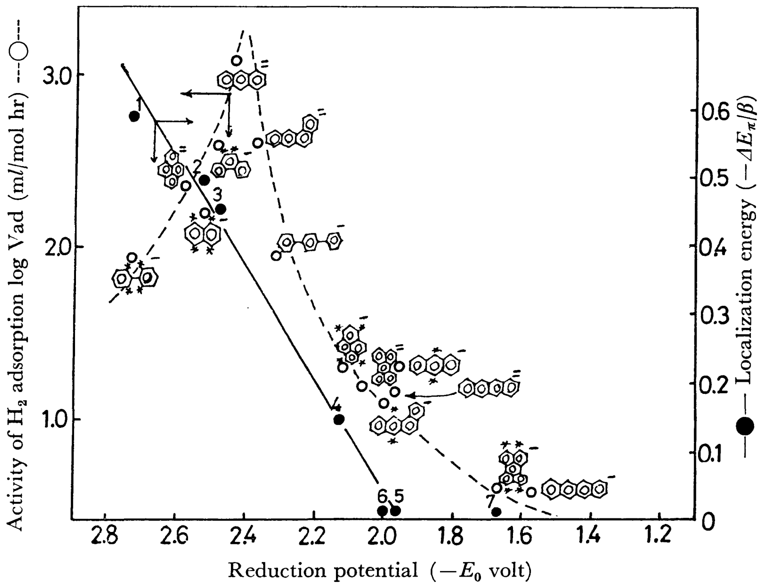

Fig. 4. The plots of the activities of hydrogen adsorption over various mono- and di-anion complex films with sodium against their reduction potentials $(-E_0$ volt), ---○---, and the plot of the localization energies of each acceptor molecules against the reduction potential of their mono-anions, —●—: 1) biphenyl 2) naphthalene 3) phenanthrene 4) pyrene 5) anthracene 6) 1,2-benzanthracene 7) perylene.
The asterisk (*) shows the position of the minimum localization energy in each of the anions of the corresponding aromatic hydrocarbons.

$$A + e \longrightarrow A^- \quad -E_1'$$
$$A^- + e \longrightarrow A^= \quad -E_2'$$

From these results it may be suggested that generally such EDA complexes which contain electron-donating anions with higher reduction potentials react readily with molecular hydrogen to cause a dissociative adsorption of hydrogen.

For the 1 : 1 and 1 : 2 complexes of pyrene, anthracene, 1,2-benzanthracene, perylene, and tetracene with sodium, each of these 1 : 2 complexes was about ten times as active as the corresponding 1 : 1 complex in the uptake of hydrogen. This can be reasonably understood in terms of the higher electron-donating properties of their di-negative ions than those of mono-anions.

It is also interesting to note in Fig. 4 that the activities of the EDA complexes with comparatively weak acceptors such as biphenyl, naphthalene, and phenanthrene, were lower in the hydrogen uptake that were expected from their reduction potentials. These acceptors have characteristically larger localization energies, as is presented in Fig. 4 to the right ordinate, where each localization energy has been calculated by the SCF MO method.[6] Accordingly, their lower activities for the hydrogen adsorption might be due to their difficulty in localizing an unpaired electron at the active position in the anions, in spite of their strong electron-donating properties.

A similar correlation was observed for the relative activities of the solutions of various complexes in connection with the reduction potentials of those anions. When hydrogen (10—45 cmHg) was introduced onto the 1:1 and 1:2 complex solutions (*ca.* 3

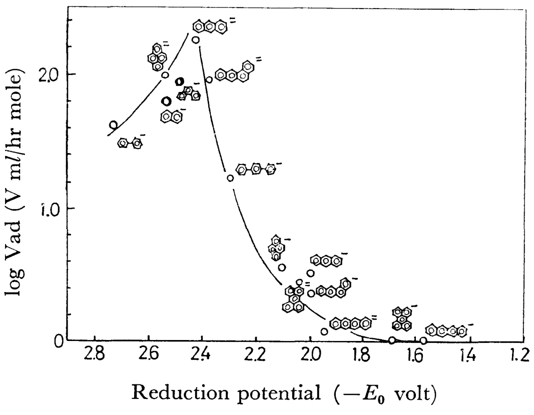

Fig. 5. The plot of the activities of the hydrogen-uptake onto the THF solution of various 1:1 and 1:2 complexes (*ca.* 3×10^{-3} mol/50 m*l* of THF) at 20°C and $P_{H_2}=20$ cm Hg against the reduction potentials of these anions.

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[6] G. Dallinga, A. A. V. Stuart, P. J. Smit and E. L. Mackor, *Z. Elektrochem.*, **61**, 1019 (1957).

$\times 10^{-3}$ mol) of biphenyl, naphthalene, phenanthrene, anthracene, 1,2-benzoanthracene, pyrene, perylene, and tetracene with sodium in THF or DME, a considerable amount of hydrogen was adsorbed in the temperature range between 20 and 45°C over 20-hr period. The relative amount of hydrogen uptake by each complex solution in THF at 20°C in 20 hr[*4] is plotted in Fig. 5.

For the 1 : 1 complexes of biphenyl, naphthalene and phenanthrene with sodium, these THF solutions were gradually decolorized with the progress hydrogen adsorption, and a considerable amount of NaH was precipitated and almost completely converted in several days to a neutral molecule and dihydro-species.[*5]

III. The Behavior of Adsorbed Hydrogen over A^-Na^+ and $A^=2Na^+$ Films or Solutions.

In order to study the change in the electronic properties of the EDA complexes in reactions with hydrogen, each of the A^-Na^+ and $A^=2Na^+$ films of various aromatic hydrocarbons with sodium was deposited[*6] from their THF solutions onto the wall of a quartz cell by evaporating the solvent; hydrogen was then admitted onto their films at the reaction temperatures.

As is shown in Fig. 6a, when hydrogen (10—40 cmHg) was admitted onto the phenanthrene$^-$Na$^+$ complex films at temperatures from 20 to 90°C, the absorption peak at 620 mμ gradually decreased at 60°C for several hours and new, broad adsorption peaks appeared at 440 and 580 mμ. When the temperature was raised to 90°C, the new peak increased in intensity, while a small amount of neutral phenanthrene was separated. On the other hand, the phenanthrene$^-$Na$^+$ film, which adsorbed hydrogen sufficiently, was dissolved in THF in an NMR tube. An intense peak appeared at t=8.73 ppm in the NMR spectra; it was attributed to that of sodium hydride much as has previously been described.[4]

In addition, when hydrogen was admitted onto the phenanthrene$^-$Na$^+$ deposited on an ESR tube, the spin concentration of the complex film (g=2.0036) decreased markedly and became almost diamagnetic upon hydrogen adsorption at 60°C for several days.

It was also found that, by introducing hydrogen into the phenanthrene$^-$Na$^+$ solution of THF, a similar absorption spectra newly appeared in the temperature range between 20 and 45°C for several hours, as is shown in Fig. 6b. It should intensity gradually and that a small amount of sodium hydride was precipitated in the solution.

The peaks which newly appeared upon hydrogen adsorption were attributed to the 9-monohydrophenanthrenium anion complex by means of a comparison with those of the 9-monohydrophenanthrenium cation,[7b] as in the case of the 1 : 1 and 1 : 2 anthracene-sodium complexes.[4] These results suggest that hydrogen adsorption proceeded on the phenanthrene$^-$Na$^+$ film as well as in its solution as follows:

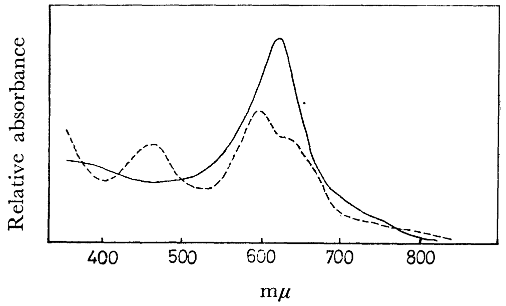


Fig. 6a. The change of the electronic spectra of the phenanthrene$^-$Na$^+$ film by the hydrogen adsorption. The solid line= that of the phenanthrene$^-$Na$^+$ film, and the dotted line= that after the hydrogen adsorption on the complex film at 60°C in 20 hr.

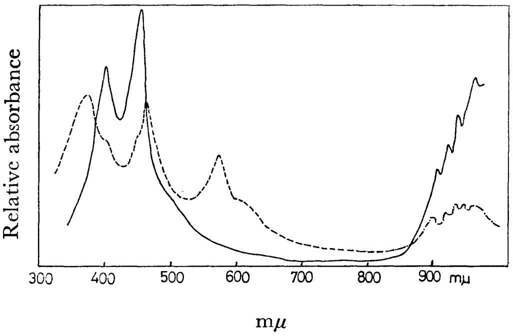


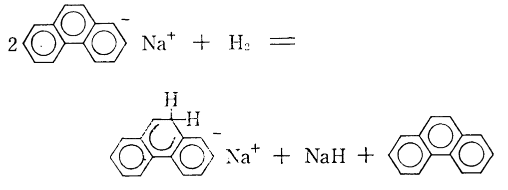
Fig. 6b. The electronic spectra of the THF solution of phenanthrene$^-$Na$^+$ (———) and after the uptake of the hydrogen at 20°C for 20 hr (---------).

[*4] The hydrogen adsorption proceeded in almost first-order kinetics in the initial stage, as is shown in Fig. 2.

[*5] After a complete reaction with hydrogen, the THF solutions of these complexes were examined by NMR spectrometry at 20°C.

[*6] The electronic absorption spectra of the complex films were comparatively broad and were considerably different from those of the corresponding complex solutions in THF or DME. This change in the spectra occurred reversibly; it is seemingly to be attributed to the formation of the anion dimer in a solid or condensed phase.

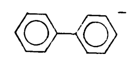
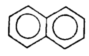
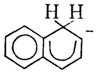
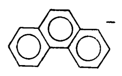
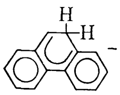
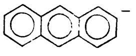
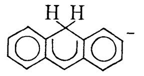
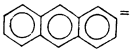
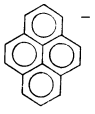
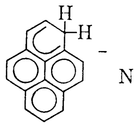
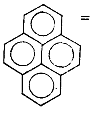
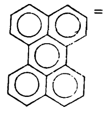
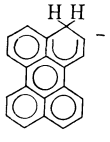
7) a) G. Dallinga, E. L. Mackor and A. A. V. Stuart, *Mol. Phys.*, **1**, 123 (1958); E. L. Mackor, G. Dallinga, J. H. Kruizinga and A. Hofstra, *Rec. Trav. Chim. Pays-Bas*, **75**, 836 (1956). b) N. H. Velthorst and G. J. Hoijtink, *J. Amer. Chem. Soc.*, **87**, 4529 (1965).



For the 1 : 1 and 1 : 2 complexes of other aromatic hydrocarbons, such as biphenyl, naphthalene, pyrene, anthracene, perylene, 1,2-benzanthracene, and tetracene with sodium, it was found similarly, in the UV, NMR and ESR measurements, that new and characteristic absorption spectra were observed after introducing hydrogen gas onto each of the complex films or THF solutions at temperatures of 20 and 90°C. The results are summarized in Table 2a for the hydrogen adsorption on the complex films and in Table 2b for that on the complex solutions. In Table 2a the positions of the absorption peaks newly appearing upon the hydrogen adsorption, the detection of sodium hydride, and the structures of the monohydroanion complexes (AH^-Na^+)*[7] in the hydrogen-adsorbed species are also presented. In Table 2b there are also the absorption peaks of the carbonium cations (AH^+) and the localization energies (L.E. $= -\Delta E\pi/\beta$) at each carbon atom in a given anion of aromatic hydrocarbons.

These results confirm that the adsorbed hydrogen was combined with the carbon atom of the mono- or di-anion at the position which has the lowest localization energy to form the corresponding monohydroanion complexes (AH^-Na^+), and that NaH was also formed simultaneously with the hydrogen adsorption.

TABLE 2a (film)

A^-Na^+, $A2Na^+$	The characteristic absorption peaks (complex films)	(on H_2-ads.)*	The probable structures of AH^-Na^+**	NaH***
 Na^+	380 mμ	—	—	+++
 Na^+	380	450 mμ	 Na^+ (unstable)	+++
 Na^+	620	440 580	 Na^+	+++
 Na^+	720	420	 Na^+	+
 $2Na^+$	620			++
 Na^+	500	430 520	 Na^+	+
 $2Na^+$	610			++
 $2Na^+$	530	470	 Na^+	+

* New absorption peaks appeared by the H_2-adsorption on each of these complex films.

** The structures of the AH^-Na^+ in the H_2-adsorbed species were predicted from their characteristic new absorption peaks in comparison with those of the corresponding carbonium ions.[7a,7b)]

*** The relative amount of NaH in the H_2-adsorbed species, which was detected by the NMR-spectra at 8.73 ppm: +++ very large ++ large + detectable

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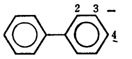
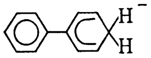
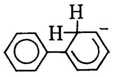
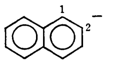
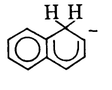
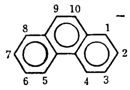
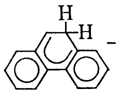
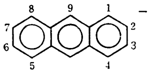
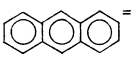
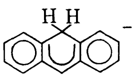
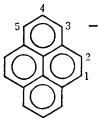
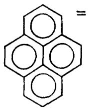
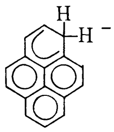
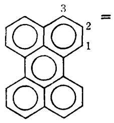
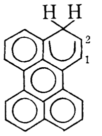
[7] The structures of several monohydroanions have been discussed in comparison with those of the corresponding carbonium ions; *e. g.*, see Ref. 7b.

TABLE 2b (solution)

A^-Na^+, $A^=2Na^+$	new peaks by H_2 ads. (mμ)	AH^-Na^+	$AH^+BF_4^-$*	L.E.** ($-\Delta E/\beta$)
 Na^+	425 (s)	 Na^+	380 (s)	2 0.59 3 0.88 4 0.61
	500 (s)	 Na^+	445 (s)	
 Na^+	435 (s) 465 (w)	 Na^+	390 (s) 280 (w)	1 0.50 2 0.73
 Na^+	360 (s) 450 (s) 580 (w)	 Na^+	280 (s) 410 (s) 520 (s)	4 0.54 3 0.58 2 0.67 1 0.45 9 0.45
 Na^+  $2Na^+$	432 (vs)	 Na^+	408 (vs)	1 0.31 2 0.57 9 0.01
 Na^+  $2Na^+$	430 (vs) 540 (s)	 Na^+	385 (s) 460 (s)	3 0.15 1 0.37
 $2Na^+$	460 (s)	 Na^+	410 (s) 600 (s)	3 0.03 1 0.13

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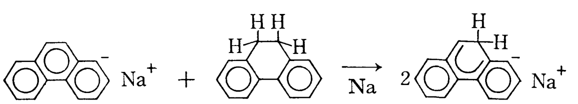
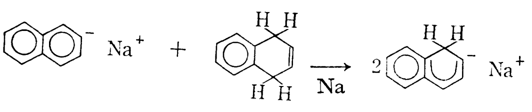
* The absorption peaks of the carbonium ions (AH^+) were obtained from the mixed solutions of a given aromatic hydrocarbon(A) and $HF+BF_4$ solution.[7a)]

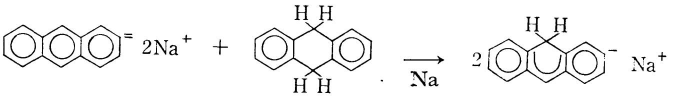
** Localization energy used has been calculated for the corresponding carbonium ions (AH^+): see Ref. 6.

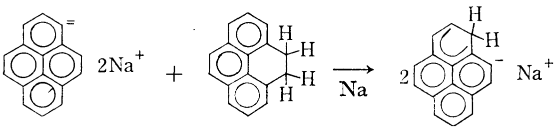
It should be noted here that biphenyl$^-$Na$^+$ complex in the THF solution slowly changed to monohydro-anion by abstracting hydrogen from the solvent even in the absence of hydrogen gas.

In addition, AH^-Na^+ was also prepared independently by the following reactions in THF and the similar absorption peaks (AH^-Na^+) were observed in the resultant solutions.









It may also be suggested that the same monohydro-anion complex was produced in the hydrogen adsorption over the A^-Na^+ and $A^{=}2Na^+$ films and the solutions of pyrene, anthracene,[4] perylene, and 1,2-benzathracene with sodium.

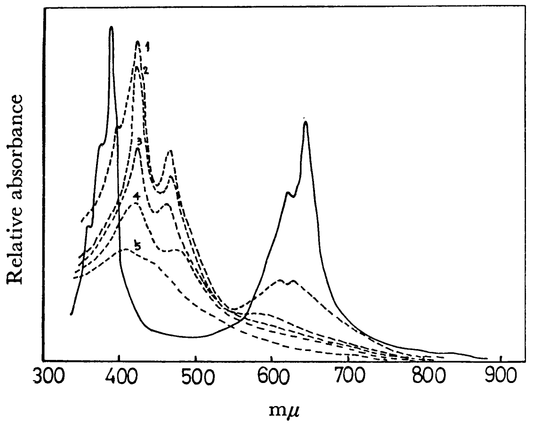


Fig. 7. The change of the electronic spectra of the biphenyl$^-Na^+$ solution in THF (———) after introducing H_2 at 20°C: (---------).
1) 10 min after 2) 20 min 3) 40 min 5) 200 min

For the biphenyl$^-Na^+$, it was found that no absorption peaks were newly observed upon introducing hydrogen on the complex film, even at higher temperatures. However, as is shown in Fig. 7, when hydrogen was admitted onto the THF solution at 20°C for several hrs, two new peaks appeared, at 425 and 490 mμ; these peaks may be attributed to the para- and ortho-monohydro-biphenyl anion respectively. These peaks decreased, however, at a considerable rate, and disappeared completely within several hrs, probably because to their decomposition, as follows:

$$AH^-Na^+ \longrightarrow A + NaH$$

$$2AH^-Na^+ \longrightarrow A + AH_2$$

For the tetracene$^{=}2Na^+$ complex, we found neither any appreciable change in the absorption spectra of the tetracene dianion nor the formation of sodium hydride upon the introduction of hydrogen in the temperature range between 20 and 120°C for several days. It was, however, demonstrated that a small and broad peak could be detected at 490 mμ[*8] after hydrogen treatment at 140°C for 10 days. It has previously been reported[8] that the proton complex of tetracene ($AH^+BF_4^-$) has an absorption peak at 448 mμ. The same absorption peak at 490 mμ could be observed in the slow reaction between tetracene$^{=}2Na^+$ and 9,10-dihydrotetracene at room temperature; this suggests that the new peak at 490 mμ can be attributed to the formation of the 9-monohydrotetracenium anion complex.

Therefore, these results suggest that a possible mechanism for the hydrogen activation by the A^-Na^+ and $A^{=}2Na^+$ is an electron transfer from mono- or di-anions to molecular hydrogen to form hydride and a hydrogen atom, which is then combined with each anion (A^-) to form the corresponding monohydro anion complexes (AH^-Na^+) as follows:

$$A^{=}2Na^+ + H_2 = A^-Na^+ + NaH + H$$

$$A^-Na^+ + H = AH^-Na^+ \qquad (1')$$

$$A^-Na^+ + H_2 = A + NaH + H$$

$$A^-Na^+ + H = AH^-Na^+ \qquad (2')$$

For the naphthalene$^-Na^+$ complex in the solution, a mechanism similar to (2′) has been proposed by Bank and his coworkers.[9] There has, however, been no crucial evidence to indicate a hydrogen atom in these reaction systems, probably because its life is too short for it to combine with radical anions (A^-).

[*8] When the film adsorbed hydrogen was dissolved in THF, a comparatively strong absorption peak appeared at 498 mμ.

[8] A. A. V. Stuart and E. L. Mackor, *J. Chem. Phys.*, **26**, 826 (1958).

[9] S. Bank, T. A. Lois, and M. C. Priolopski, *J. Amer. Chem. Soc.*, **91**, 5407 (1969).