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Mechanism of Hydrogen Exchange Reactions on 1:2 Electron Donor-Acceptor Complexes of Anthracene with Sodium

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The mechanisms of the H_2–D_2 and D_2–HZ exchange reactions over 1:2 Electron Donor-Acceptor (EDA) complexes of anthracene with sodium, where HZ denotes the EDA complexes, were studied kinetically and spectroscopically in the temperature range 20—90°C. It was found that molecular hydrogen exchanges directly with the hydrogen of the complexes ($An^{2-}2Na^+$ or An^-Na^+) and also with the monohydroanion complex (AnH^-Na^+), which is formed by the dissociative adsorption of hydrogen. The H_2–D_2 exchange reaction proceeded *via* not only the σ-bonded hydrogen of the complexes, but also homolytically dissociated "mobile" hydrogen.

The reactions of hydrogen over various electron donor-acceptor (EDA) complexes of various aromatic compounds, such as aromatic hydrocarbons, their substituted compounds[1a] and phthalocyanines,[1b] with alkali metals were studied previously. It was found that H_2–D_2 and D_2–HZ exchange reactions (HZ denotes the EDA complexes) took place at room temperature at considerable rates, hydrogen being dissociatively adsorbed. It is of interest to elucidate the reasons for this reactivity which appears on the formation of the EDA complexes.

The composition of the complexes studied so far[1a] was not always well defined. In this study, however, stoichiometric complex films were employed, and the role of the chemisorbed hydrogen on the EDA complexes was studied. The active intermediates for the hydrogen exchange reactions were determined by NMR and UV spectroscopic techniques.

Experimental

Stoichiometric complex films of anthracene with sodium ($An^{2-}Na^+$ and An^-Na^+: An=anthracene) were prepared from their stoichiometric tetrahydrofuran (THF) solutions by evaporating the solvent.[2,3]

The formation and composition of the complexes as films or in solution[4] were confirmed by their characteristic absorption spectra. The complex films were evacuated at about 100°C for one day, prior to the experiments. Anthracene was purified by repeated recrystallization and the zone-melting method. Sodium was purified by distillation. In the hydrogen exchange reactions the isotopic hydrogen mixtures were analyzed by gas chromatography using an activated alumina column.

The reactions were carried out in a closed circulating system, which included a U-type reaction vessel.

Results and Discussion

Hydrogen Exchange Reaction between D_2 and the Hydrogen of 1: 2 Anthracene-sodium Complex Film (D_2–HZ Exchange

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[1a] M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, **63**, 997, 2015 (1967); *J. Catal.*, **6**, 336 (1966), **9**, 418 (1968); This Bulletin, **40**, 1050, 1294 (1967).

[1b] M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru; *Trans. Faraday Soc.*, **63**, 1215 (1967); This Bulletin, **41**, 1739 (1968).

[2] S. Tanaka, M. Ichikawa, S. Naito, M. Soma, T. Onishi, and K. Tamaru, This Bulletin, **41**, 1278 (1968).

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

[4] M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, *J. Amer. Chem. Soc.*, **91**, 6505 (1969).

Reaction). When D_2 (40 cmHg) was introduced onto the film of $An^{2-}2Na^+$, 5.6×10^{-3} mol, at temperatures between 20 and 90°C, a considerable amount of D_2 was adsorbed, and at the same time the gaseous deuterium was diluted by hydrogen from the complex forming HD in the gas phase, as shown in Fig. 1.

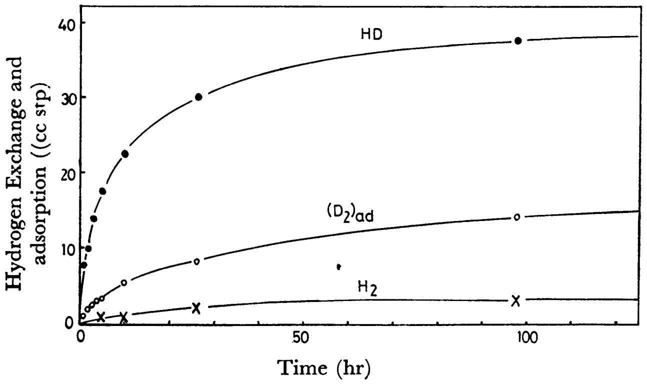


Fig. 1. The kinetics of the D_2-HZ exchange reaction and the hydrogen adsorption $(D_2)_{ads}$ over $An^{2-}2Na^+$ complex film at 80°C, $P_{D_2}=40$ cmHg.

The hydrogen adsorbed over the $An^{2-}2Na^+$ film could be completely removed by evacuating the system at 100°C for 20 hr. Reproducible results were obtained for the D_2–HZ reaction and the hydrogen adsorption.

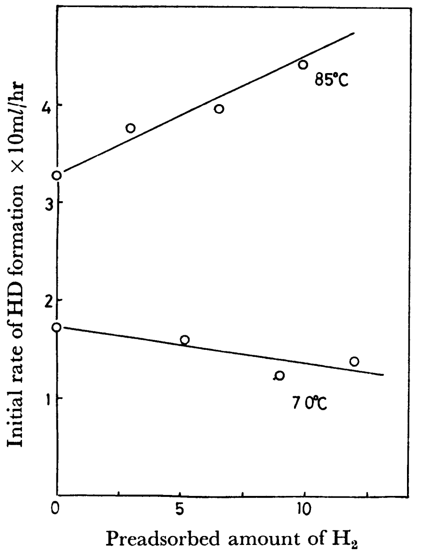


Fig. 2. Intial rates of HD formation *versus* the amount of preadsorbed hydrogen, $(H_2)_{abs}$ over an An^{2-} $2Na^+$ film (5×10^{-3} mol). $P_{D_2}=20$ cmHg.

The behaviour of the hydrogen adsorbed on the $An^{2-}2Na^+$ film in the hydrogen exchange reaction was examined at temperatures between 25 and 85°C, and by admitting D_2 (20 cmHg) onto a film (5×10^{-3} mol) deposited on silica wool on which various amounts of H_2 (from 2 to 42 m*l* stp) had been preadsorbed. The desorption of hydrogen was very slow at lower temperatures. We see from the results given in Fig. 2 that at lower temperatures (25 to 70°C) the rate of HD formation decreased slightly with increasing amounts of preadsorbed hydrogen. On the other hand, at higher temperatures such as 85°C, the rates increased slightly with increasing amount of the preadsorbed hydrogen. The initial rates of HD formation for all temperatures extrapolated to zero H_2 adsorption are not zero, but correspond to those observed over the fresh $An^{2-}2Na^+$ films. These results suggest that at least in the initial stage of the reaction the D_2–HZ exchange reaction takes place directly between the gas phase D_2 and the hydrogen of the $An^{2-}2Na^+$ complex, not through the hydrogen chemisorbed on the complex. This is also supported by the fact that the rate of HD formation was faster than that of D_2 adsorption (Fig. 1).

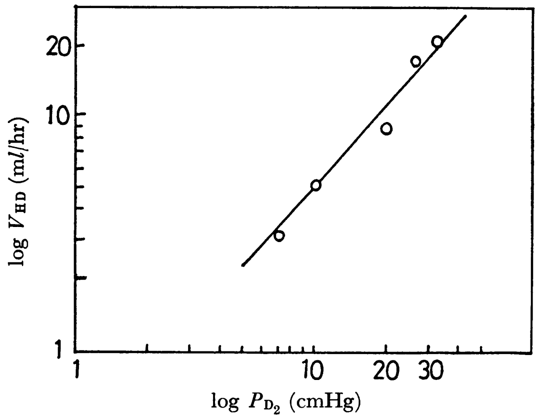


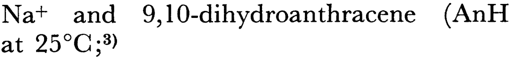
Fig. 3a. Dependence of the D_2-$(H_2)_{ads}$ exchange reaction rate upon the deuterium pressure over An^{2-} $2Na^+$ which had been adsorbed with H_2 (42 cc stp) at 62°C.

The exchange reaction between D_2 (20 cm) and an almost saturated adsorbed hydrogen layer, $[(H_2)_{ads}/(An^{2-}2Na^+)_0=0.9]$ was studied at temperatures between 20 and 90°C. Near saturation the kinetics of the HD formation were represented by the following equation (Fig. 3a).

$$-\mathrm{d(HD)}/\mathrm{d}t = kP_{D_2}(H_2)_{ads}$$

To determine the position of the hydrogen taking part in the D_2–HZ exchange, the complex film was decomposed by oxygen after exchange with D_2, and the resulting anthracene was analyzed by mass and NMR spectrometry. The results suggested that the mono-deuterated (9-position of the anthracene) product was obtained in the initial exchange ($d_0=80$, $d_1=18$, $d_2=2$, $d_3=0\%$).

As was suggested previously,[2,3)] 9-monohydroanthracenium sodium (AnH^-Na^+) and sodium hydride were produced by hydrogen adsorption over the $An^{2-}2Na^+$ film.



AnH^-Na^+ was also separately prepared by reacting $An^{2-}2Na^+$ and 9,10-dihydroanthracene (AnH_2) in THF at 25°C;[3)]

$$An^{2-}2Na^+ + AnH_2 = 2AnH^-Na^+$$

The AnH^-Na^+ thus prepared (identified by its charac-

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5) M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, This Bulletin, **43**, 3672 (1970).

teristic electronic absorption band at 432 mμ) was deposited on the wall of the reaction vessel (270 m*l*) by evaporating the solvent at 25°C. The film of $AnH^{-}Na^{+}$ was stable at temperatures below 80°C, but when strongly evacuated for several hours above 80°C it slowly changed to the monoanion anthracene complex by giving off hydrogen;

$$2AnH^{-}Na^{+} = 2An^{-}Na^{+} + H_2$$

When 20 cmHg of D_2 was introduced onto the $AnH^{-}Na^{+}$ film at temperatures between 20 and 80°C, the reversible HD formation proceeded following first-order kinetics, and attained an equilibrium value. The apparent activation energy for the hydrogen exchange between D_2 and the $AnH^{-}Na^{+}$ film was determined to be 10 kcal/mol. It was also found that at 65°C the rate of HD formation in the D_2–$AnH^{-}Na^{+}$ exchange reaction was proportional to the pressure of D_2 (6.5 to 45 cmHg) and to the amount of exchangeable $AnH^{-}Na^{+}$ (Fig. 3b).

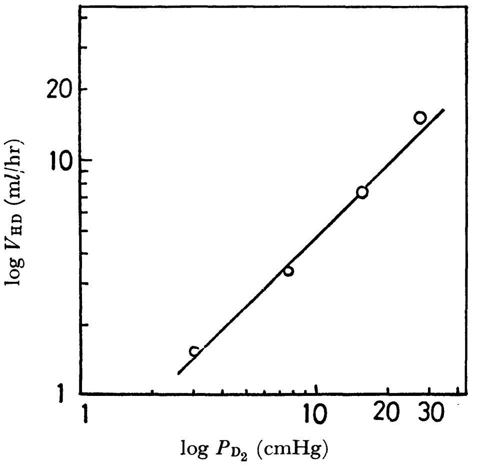
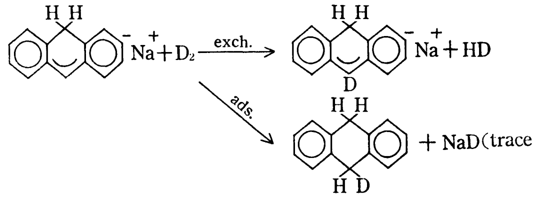


Fig. 3b. Depencence of the D_2-$AnH^{-}Na^{+}$ exchange reaction rate upon the deuterium pressure at 65°C.
$AnH^{-}Na^{+}$ (7×10^{-3} mol)

$AnH^{-}Na^{+}$ dissolved in d_8-tetrahydrofuran (from Merck Co., 98% pure) was completely exchanged with D_2 at 65°C, and the complex solution was analyzed by NMR spectrometry. It was found that the deuterium exchange took place selectively at the 10-position of the 9-monohydroanthracenium sodium, and a small amount of monodeuterated 9,10-dihydroanthracene was formed in the resulting solution. Interpretation of the spectra was carried out using the results obtained by Schneider.⁶⁾ The deuterium exchanged monohydroanthracene was evacuated ($AnH^{-}Na^{+}=An^{-}Na^{+}+1/2\ H_2$), decomposed by oxygen, collected by sublimation and analyzed by mass and NMR spectrometry. It was shown that monodeuterio(9-position) anthracene was the major product.

$$d_0\text{-anthracene}=10,\ d_1=88,\ d_2=2,\ \text{and}\ d_3=0\%$$

The results seem to indicate that the monohydroanthracenium complex participates in the hydrogen exchange reaction at the carbon atom opposite to the one where hydrogen was added, and during the course of the hydrogen exchange reaction desorption of the added hydrogen takes place rather slowly. Thus, only the d_1 species is produced to any extent by the deuteration, and no marked mixing at two equivalent carbon atoms (9- and 10-positions) was observed. From these results it is suggested that the D_2–$AnH^{-}Na^{+}$ exchange reaction proceeds as follows.



To clarify the role of the NaH in the hydrogen exchange reaction, a slight excess sodium hydride (or NaD) (75 mg, 3×10^{-3} mol) was added to the $AnH^{-}Na^{+}$ (2.8×10^{-3} mol) in THF, and a mixed film of $AnH^{-}Na^{+}$ and NaH was thus deposited on silica wool (The hydrogen exchange reaction did not proceed over the NaH alone under these reaction conditions).

The hydrogen exchange reaction was carried out in the three different systems as follows:

$$(AnH^{-}Na^{+},\ NaH) + D_2 \longrightarrow HD \quad d(HD)/dt = r_1$$

$$(AnH^{-}Na^{+},\ NaD) + D_2 \longrightarrow HD \quad r_2$$

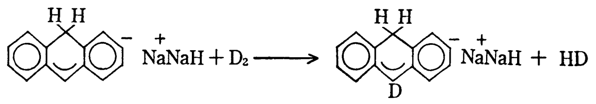
$$(AnH^{-}Na^{+},\ NaD) + H_2 \longrightarrow HD \quad r_3$$

where $AnH^{-}Na^{+}$ (3×10^{-3} mol) and AnH or NaD (*ca.* 1 g, 4×10^{-2} mol) were employed to make the mixed films. The rates, r_1 and r_2, were found to be almost equal (*ca.* 4 m*l*/hr), whereas r_3 was negligibly small at 65°C under the same reaction conditions.

When an adduct film of $AnH^{-}Na^{+}$ (3×10^{-3} mol) and NaD (*ca.* 4×10^{-2} mol) was heated at 85°C for several hours *in vacuo*, a small amount of hydrogen gas was collected. Gas chromatographic analysis gave its composition as $H_2=2\%$, $HD=87\%$, and $D_2=11\%$. From UV-spectroscopic measurements it was found that $An^{2-}2Na^{+}$ was regenerated and $AnH^{-}Na^{+}$ decreased by eliminating hydrogen:

$$AnH^{-}Na^{+} + NaD \longrightarrow An^{2-}2Na^{+} + HD$$

The results suggest that it is the hydrogen in the $AnH^{-}Na^{+}$ which participates in the exchange with molecular hydrogen, the hydrogen of NaH being unreactive for the exchange reaction at the temperatures studied.



It was therefore concluded that the overall process for the D_2–HZ exchange reaction occurred simultaneously with D_2 adsorption on the $An^{2-}2Na^{+}$ film as follows.

i) Direct hydrogen exchange between $An^{2-}2Na^{+}$ and D_2 accompanied by dissociative chemisorption:

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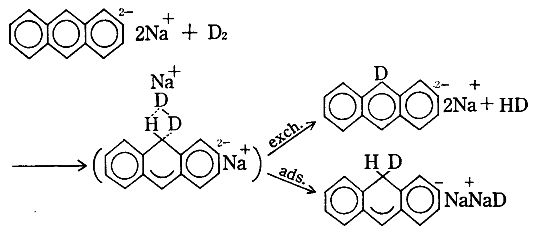
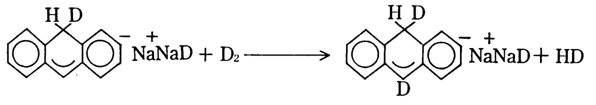
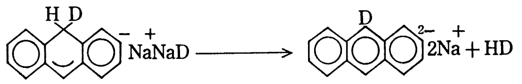
6) W. G. Schneider, Nucl. Magnetic Resonance Chem. Proc. Symp., (Cagliari, Italy, 1964).



ii) Direct hydrogen exchange of D_2 with AnD^-Na^+ which was formed by the D_2 adsorption:



iii) At temperatures above 85°C the desorption process also contributes to the hydrogen exchange reaction, *viz.*,



The H_2–D_2 Exchange Reaction over the 1:2 Anthracene-sodium Complex Film. When a 1:1 mixture of H_2 and D_2 (total pressure 20 cmHg) was admitted onto a fresh $An^{2-}2Na^+$ film (5.2×10^{-3} mol) deposited on silica wool, HD was produced and total deuterium content in the gas phase decreased as shown in Fig. 4.

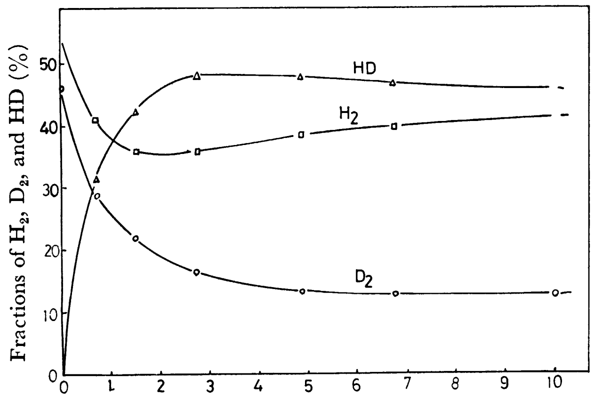


Fig. 4. The kinetics of the H_2-D_2 exchange reaction over an An^{2-} $2Na^+$ film (5.2×10^{-3} mol) at 82°C. $p_{H_2+D_2}=20$ cmHg.

The initial rate of HD formation in the H_2–D_2 exchange reaction was studied after the complete evacuation of the residual adsorbed hydrogen and was compared with that of the D_2–HZ reaction, which lead to the following conclusions: Above 82°C the temperature dependence and the initial rate of HD formation from a H_2–D_2 mixture were similar to those of the D_2–HZ exchange reaction ($P_{D_2}=20$ cmHg) as shown in Fig. 5. The HD formation in the H_2–D_2 exchange reaction thus results mainly from the following two exchange reactions which involve the bonded hydrogen of the $An^{2-}2Na^+$ complex.

$$D_2 + HZ = HD + DZ$$

$$H_2 + DZ = HD + HZ$$

HZ: $An^{2-}2Na^+$ or AnH^-Na^+

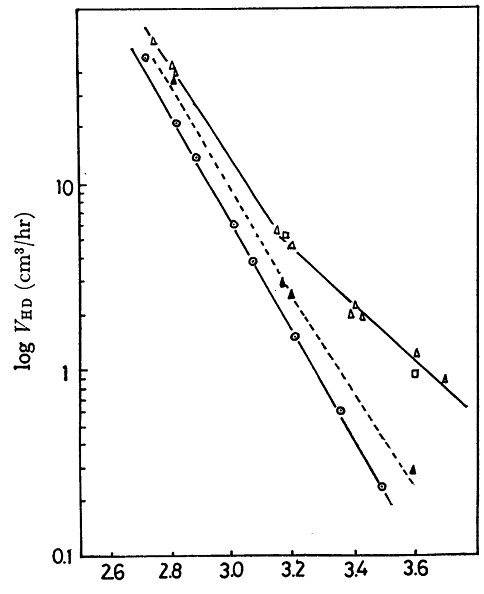


Fig. 5. Arrhenius' plot for the initial HD formation in the H_2-D_2 exchange reaction over $An^{2-}2Na^+$ films (-△-△-), and in the D_2HZ (HZ=$An^{2-}2Na^+$) excahnge reaction (-○-○-). The rates of HD formation in the H_2-D_2 exchange reaction after the preadsorption of CO (*ca.* 4.5 cc) (-▲-▲-), and after evacuation of the preadsorbed CO from the complex film (-□-□-).

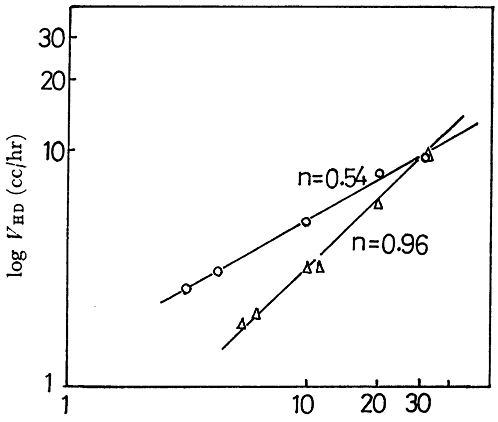


Fig. 6. Dependence of the H_2-D_2 exchange reaction rate upon the total pressure of H_2+D_2 (1:1) mixture and the deuterium pressure ($P_{H_2}=10$ cmHg) over $An^{2-}2Na^+$ (5.2×10^{-3} mol) film at 45°C.
-○- log P_{D_2} (cmHg) -△- log $P_{H_2+D_2}$ (cmHg)

On the other hand, at lower temperatures, *e.g.* 42°C, the HD formation from a H_2–D_2 mixture was faster than in the D_2–HZ exchange reaction (Fig. 5). The initial rate of HD formation could not be explained by the above mentioned bonded mechanism alone and the H_2–D_2 exchange reaction almost reached thermal equilibrium in the gas phase. The pressure dependence of the rates of the H_2–D_2 exchange reaction at 45°C was found to be proportional to the total pressure of the H_2–D_2 mixture (1: 1), and to the square root of each of the H_2 and D_2 pressures as shown in Fig. 6.

$$d(HD)/dt = kP_{H_2}^{1/2}P_{D_2}^{1/2}$$

It is thus suggested that at lower temperatures the

H_2–D_2 exchange reaction takes place mainly *via* the recombination of "mobile" hydrogen chemisorbed on the complex film:

$$\left.\begin{array}{l} D_2 \rightleftarrows 2D(a) \\ H_2 \rightleftarrows 2H(a) \end{array}\right\} \rightleftarrows 2HD$$

It should be noted that when the $An^{2-}2Na^+$ film adsorbed carbon monoxide (4.5 and 16 m*l* stp) at 40°C, the HD formation from the H_2–D_2 exchange reaction decreased markedly, and the initial rates of HD formation became almost equal to those obtained at similar temperatures for the D_2–HZ exchange reaction. After evacuation of the complex film at 85—100°C for 20 hr, the activity of the film for the H_2–D_2 exchange reaction was completely restored as shown in Fig. 5. It is suggested that CO effectively inhibited the "weakly chemisorbed hydrogen" mechanism, but had negligible effect on the exchange between D_2 and the hydrogen of the complex molecule.