The Behavior of Hydrogen Chemisorbed over the Electron Donor-Acceptor Complexes of Aromatic Hydrocarbons with Sodium in the Hydrogen Exchange and Hydrogenation Reactions

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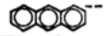
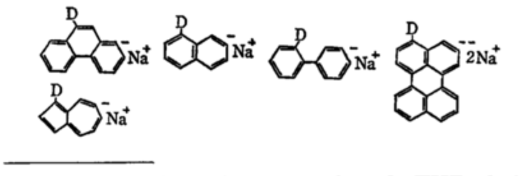
In a previous paper[1] it was demonstrated that the hydrogen molecule is activated at room temperature over the electron donor-acceptor (EDA) complexes of various organic compounds with metals such as sodium, whereas no activations took place over the organic molecules or over such metals alone.

In this experiment anthracene-Na (1 : 1 and 1 : 2) films were prepared over the glass wall of a reaction vessel in an ordinary manner.[2] The reactions were carried out over the films after evacuation had been carried out for several hours at 100°C.

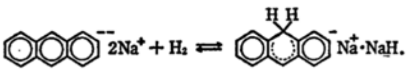
When 15 cmHg of D_2 gas was introduced onto the 1 : 1 and 1 : 2 complex films in the temperature range between 25 and 90°C, a considerable amount of HD was formed reversibly; the apparent activation energies for the reactions were approximately 16 and 12 kcal/mol respectively. The film of the anthracene-Na (1 : 2) complex was approximately ten times as active as that of the 1 : 1 complex for the hydrogen exchange. The rates of the H_2–D_2 (1 : 1) exchange reaction were of the same order of the magnitude as those of the D_2–HZ exchange reaction under similar conditions, where HZ represents the EDA complexes.

After the exchangeable hydrogens in these complexes had been replaced with deuterium to a considerable extent by treating the complexes with deuterium gas at 80°C, the deuterated positions in these complexes were studied by means of the ESR and NMR techniques, which revealed that the hydrogen at the 9 or 10 position of  and  was only exchanged with deuterium. The deuterated position of similar EDA complexes was also studied in a similar manner. It was consequently found that the exchange reaction took place at the following positions:



The positions where the exchange reaction took place were those with the lowest localization energy in the mononegative or dinegative ions, except for the case of azulene.

By admitting the hydrogen gas onto the thin films of 1 : 1 and 1 : 2 anthracene-Na complexes, which had been prepared on the wall of a quartz cell, a new peak appeared at 432 mμ, while the peaks due to the dinegative anion and to the mononegative radical anthracene in the complexes decreased correspondingly. The new peak is seemingly due to the 9-monohydroanthracenium anion; it disappeared after evacuation had been carried out at 100° C for several hours. The ESR measurements of the complexes indicated that the total spin concentration of the 1 : 1 complex film diminished considerably upon the introduction of hydrogen onto the complex. The free spins were restored almost completely by evacuation at 100°C. When 1 : 2 complex films were treated with hydrogen gas at 90°C and were then dissolved in THF at 25°C, the resulting solutions showed a new NMR signal, at $\tau=8.73$, corresponding to H–Na.[*1] The results suggest that the hydrogen molecule attacks the 9-position of the anthracene-dinegative anion and is dissociated heterolytically in the following manner:



In this case the ambient hydrogen gas was replaced by deuterium, and the formation of hydrogen deuteride was followed with the time. It was accordingly found that almost all the hydrogens chemisorbed over the complex films participate in the exchange reaction with the ambient deuterium molecules, and the exchange rate was proportional to the amount of hydrogen adsorbed.

Monodeuteroanthracene of the 1 : 2 complex was prepared by treating the film with excess D_2 at 90°C for 2 days; subsequently the ambient hydrogen gas was replaced with dimethylacetylene, butadiene, or methylacetylene. As a consequence, a small amount of deuterated 2-butenes was selectively produced, while the peak at 432 mμ of 9-monohydroanthracene slowly decreased.

[*1] The signal was the same as that of a THF solution of sodium hydride.

1) M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, **63**, 1215, 2015, 2528 (1967).

2) G. J. Hoijtink and P. J. Zandstra, *Mol. Phys.*, **3**, 371 (1960).