

REACTIVITY OF ELECTRON DONOR-ACCEPTOR COMPLEXES.  
PART IV. HYDROGEN EXCHANGE REACTION BETWEEN ACETYLENE  
AND THE ELECTRON DONOR-ACCEPTOR COMPLEXES OF VARIOUS  
AROMATIC HYDROCARBONS WITH SODIUM.

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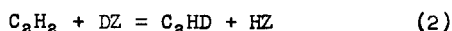
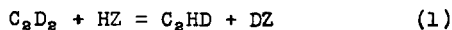
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We have previously reported (1-3) that hydrogen exchange occurs at room temperature between acetylene, or molecular hydrogen, and the electron donor-acceptor (EDA) complexes of various phthalocyanines with sodium, while the exchange did not proceed over pure phthalocyanines even at higher temperatures such as 200°C. Accordingly, the reactivity of phthalocyanines increased strikingly by forming EDA complexes with sodium, and the hydrogen atoms in the complexes can exchange with those in acetylene and molecular hydrogen. In this communication we should like to report the reactivity of EDA complexes of sodium with several ac-

ceptor aromatic hydrocarbons.

A small amount of aromatic hydrocarbons such as biphenyl, naphthalene, anthracene, phenanthrene, pyrene, and violanthrene were sublimed onto the evaporated films of sodium metal, which had been purified by repeated distillation prior to the use, and violet complexes were obtained. Violanthrene was obtained by reducing violanthrone with zinc powder and by repeated recrystallization and sublimation. The EDA complexes thus prepared were subjected to a heat treatment at 80°C for 24 hours.

When  $C_2D_2$  was introduced onto these complexes, a considerable amount of  $C_2HD$  appeared in the gas phase, the total pressure staying constant. Thus, it is demonstrated that hydrogen exchange takes place between acetylene and the complexes. The exchange reaction proceeded reversibly so that  $C_2HD$  was also produced when  $C_2H_2$  was brought into contact with the complexes which had been deuterated by  $C_2D_2$ . These observations can be accounted for by the following reactions:



where HZ represents the EDA complexes. The first-order rate constants and the activation energies of the hydrogen exchange reaction between acetylene and various com-

plexes are given in the Table.

Since the number of hydrogen atoms in acetylene gas was considerably more than that of the exchangeable hydrogen in the surface of the EDA complexes, the rate of the exchange is proportional to the concentration of the hydrogen in the surface of the complex. Consequently, the rate constants shown in the Table are independent

TABLE

Electron acceptor	First-order * rate constant (min. <sup>-1</sup> )	$k_H/k_D$ **	Activation energy (kcal/mol)
Biphenyl	$1.8 \times 10^{-2}$	1.0	4.6
Naphthalene	$3.5 \times 10^{-2}$	1.0	3.7
Anthracene	$4.0 \times 10^{-2}$	1.4	3.5
Phenanthrene	$2.8 \times 10^{-2}$	1.2	4.0
Pyrene	$0.96 \times 10^{-2}$	2.0	5.0
Violanthrene	$7.6 \times 10^{-2}$	2.4	6.8

of the surface area or the number of the exchangeable hydrogen atoms in the surface of the EDA complexes.

Upon initial contact of  $C_2D_2$  with the fresh complexes the reaction rate of the exchange was different, usually lower than the subsequent reversible exchange.

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\* The rate constant in the stationary state at 20°C under 12.5 cm Hg acetylene pressure.

\*\*  $k_H$  and  $k_D$  are the rate constants of the reactions (1) and (2) respectively.

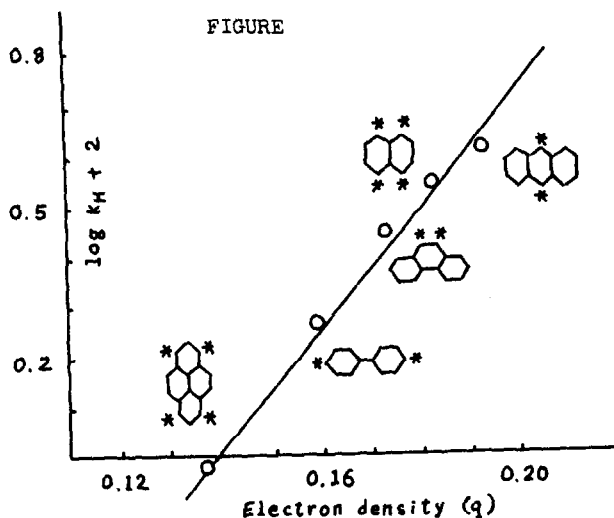
It is reproducible for fresh complexes and is not affected by the longer heat treatment of the films prior to the use. The repeated exchange on the EDA complexes showed a reproducible rate except the first experiment. These suggest that the heat treatment is sufficient to reach an equilibrium formation of the EDA complexes.

In the case of the anthracene-Na complexes, the exposure to acetylene gas resulted in a gradual decoloring, while the exchange reaction still proceeded reversibly. The resulting pale yellow solid complex was dissolved into tetrahydrofuran and was examined by NMR technique, and there appeared new absorption peaks different from those of anthracene and 9,10-dihydroanthracene. It is suggested that the  $\pi$ -conjugate system of anthracene was partly destroyed. 9,10-dihydroanthracene-sodium complex was not reactive for the exchange at room temperature. These results suggest that the exchange reaction takes place via some sigma-bonded hydrogen intermediate of the hydrocarbon.

When an electron acceptor,  $\text{SbCl}_5$ , was added to anthracene, instead of the electron donor, no exchange reaction took place with acetylene, which suggests that the exchange reaction proceeds with basic hydrogen rather than acidic hydrogen.

The rate constants given in the Table can be cor-

related with the highest electron density ( $q$ ) of the half occupied molecular orbitals of the aromatic hydrocarbon anions. This correlation is shown in the Figure, where the highest electron densities have been calculated from the Hückel LCAO method (4-6). Accordingly, the



electronegative carbon atom, or the hydrogen which attaches to it, seems to behave as an active site for the exchange reactions.

It should be noted here that when molecular deuterium was brought into contact with the EDA complexes of violanthrene, anthracene, pyrene and phenanthrene, exchange occurred and hydrogen deuteride was formed.

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