Reactivity of Electron Donor-Acceptor Complexes. VII. Hydrogen Exchange Reaction over Electron Donor-Acceptor Complexes of Aromatic Compounds

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It was previously reported[1,2] that the hydrogen exchange reaction takes place between D_2 and various electron donor-acceptor (EDA) complexes, and also that the H_2-D_2 exchange reaction to form HD proceeds with a considerable rate over the complexes. The latter exchange reaction proceeds more rapidly than is expected from the former reaction.[1] The H_2-D_2 exchange reaction, in the other hand, takes place over the EDA complexes of sodium with electron acceptors that contain no hydrogen, such as tetrachlorophthalonitrile and hexachlorobenzene. Accordingly, it was suggested that the H_2-D_2 exchange reaction over the EDA complexes proceeds *via* two different mechanisms: one involves bonded hydrogen, the other involves hydrogen "chemisorbed" on the EDA complexes, and the exchange rate of each mechanism can be calculated from the HD formation using D_2 alone and H_2-D_2 mixture respectively.

In this study, the catalytic activity for the H_2-D_2 exchange reaction *via* the chemisorption mechanism has been examined over the EDA complexes of various aromatic compounds. The experimental procedures were the same with those in the previous papers.[2] The effective surface for the hydrogen chemisorption mechanism was estimated from the exchange equilibrium between D_2 and the complex to form HD at comparatively low temperatures. The experimental conditions were controlled so that the amount of exchangeable hydrogen was of the same order of magnitude for various complexes. The actual amount of exchangeable hydrogen was used to normalize the H_2-D_2 exchange rates.

The relative first-order rate constants and the activation energies for the H_2-D_2 exchange reaction *via* chemisorption mechanism at 80°C are plotted in the figure against the electron affinity (estimated by Briegleb[3]) of acceptor molecules in the EDA complexes. EDA complexes of cyano-

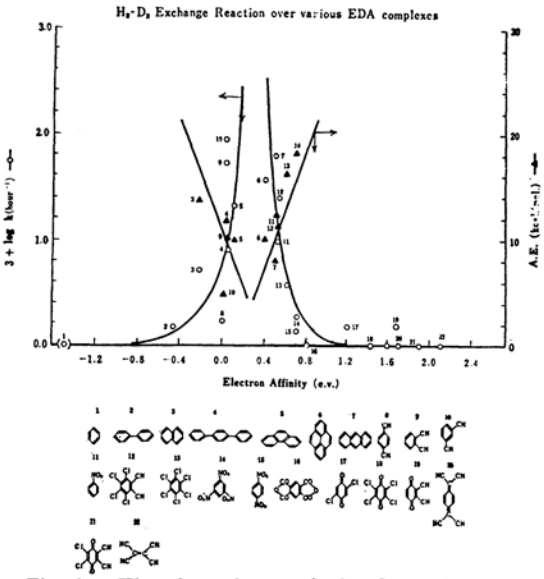

Fig. 1. The dependence of the first-order rate constant (hr^{-1}), —○—, and its activation energy, --▲--, for the H_2-D_2 exchange reaction upon the electron affinity of acceptor molecules in the EDA complexes with sodium.

naphthalene, cyanobenzene and various phthalocyanines were also considerably active, but their electron affinities are not known.

It is of great interest that the activity of the EDA complexes is strongly dependent upon the electron affinity of acceptor molecules: The activity has a maximum in the region of 0 to 0.6 eV electron affinity of the acceptor molecule and is very small or negligible for either stronger or weaker acceptor molecules.

The catalytic activity is strongly dependent upon the number of substituents of a given kind. Mononitrobiphenyl, mononitro- and monocyanonaphthalene were much more active than biphenyl and naphthalene, respectively. However, the activity of dinitrobiphenyl and 1, 5- and 1, 8-dinitronaphthalene was low, and that of tetranitropyrene was immeasurable up to 130°C. These low activities are probably due to excessively strong electron affinity.

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3) G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).