Hydrogen Exchange Reaction between Molecular Hydrogen and the Electron Donor-Acceptor Complexes of Various Aromatic Compounds

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The exchange reaction of hydrogen between acetylene, or molecular hydrogen, and the electron donor-acceptor (EDA) complexes of sodium with aromatic hydrocarbons, phthalocyanines, cyano- and nitro-substituted compounds has been studied previously.[1,2] The reactivity of such compounds increases strikingly when they are brought into contact with sodium, as an electron donor, to form EDA complexes. The hydrogen exchange reaction with acetylene proceeds *via* the bonded hydrogen in the acceptor molecules and the rate is correlated with the densities of unpaired electron in the anion radicals of acceptors in the EDA complexes.[2]

The hydrogen exchange reaction between molecular hydrogen and the EDA complexes takes place reversibly in the following manner;

$$D_2 + HZ = DZ + HD \qquad (1)$$

$$H_2 + DZ = HZ + HD \qquad (2)$$

where HZ represents the EDA complexes. The rate of this reaction has been studied by measuring the rate of formation of HD when D_2 (12.5 cmHg) was introduced onto the EDA complexes in the temperature range between 25 and 125°C. The reacting gas was analyzed by gas chromatography as described previously.[2]

In the present investigation we have shown that the rate constant for reaction (1) correlates with the maximum density of the unpaired electron in the anion radical of the acceptor molecule which densities have been calculated from the simple Hückel MO method.[3] In Fig. 1, the rate constants (hr^{-1}) at 80°C and the activation energy (kcal/mol) for the exchange reaction (1) are plotted against the maximum densities of unpaired electrons (q) in the anion radical.[4] The only exception in the correlation so far studied was the biphenyl-Na complex, the reactivity of which is very low ($k_H = 0.0026\ hr^{-1}$) in spite of the radical's medium electron density ($q = 0.158$). The hydrogen exchange, on the other hand, proceeded considerably fast over the EDA complex of 4-chlorobiphenyl ($k_H = 0.018\ hr^{-1}$) with sodium. The reason for the exceptionally low activity of biphenyl-Na complex is not clear, but it might be due to its low electron affinity (the lowest of all the acceptor studied) which results in a weak EDA complex.

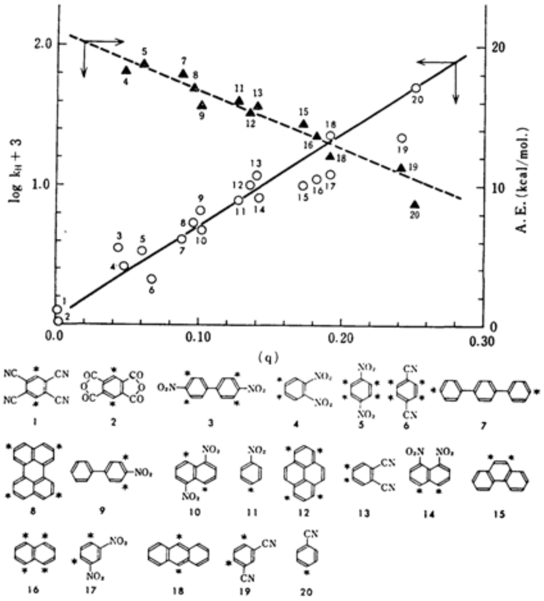

Fig. 1. Hydrogen exchange reaction between D_2 and the EDA complexes of sodium with various organic acceptors.
q: highest density of unpaired electron in anion radical
k_H: first order rate constant (hr^{-1})

It is demonstrated in the figure that the exchange rate is higher at the carbon atoms of higher electron densities in the acceptor molecules.

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[1] T. Kondow, H. Inokuchi and N. Wakayama, *J. Chem. Phys.*, **43**, 3766 (1965); Catalysis Meeting, Sapporo, Japan, Sept., 1966.

[2] M. Ichikawa, M. Soma, T. Onishi and K. Tamaru, *J. Phys. Chem.*, **70**, 2069, 3020 (1966); *J. Catalysis*, **6**, 336 (1966); *Tetrahedron Letters*, **47**, 5841 (1966).

[3] A. Carrington and P. F. Todd, *Mol. Phys.*, **6**, 161 (1963); P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962); A. Carrington and J. Dos Santos-Veigu, *Mol. Phys.*, **6**, 273 (1963); K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); P. H. Rieger and G. K. Fraenkel, *ibid.*, **39**, 609 (1963); E. Brunner, R. Mücke and F. Dörr, *Z. physik. Chem.*, **50**, 30 (1966).

[4] The asterisks * in the figure denote the position of the highest electron density in each of the anion radical.