The Reactivity of Electron Donor-acceptor Complexes. The Effect of the Complex Formation on the Reduction of Methylene Blue in the Presence of Aromatic Hydrocarbons

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The hydrogen transfer from dihydro-aromatic hydrocarbons to methylene blue was chosen for study, with methylene blue being regarded as a model compound of flavin co-enzymes, and the effect of aromatic hydrocarbons added was studied.

Various aromatic hydrocarbons, such as naphthacene, perylene, anthracene, and pyrene, were purified by recrystallization and sublimation, while commercial methylene blue and dihydro-aromatic hydrocarbons, such as 9,10-dihydroanthracene, 9,10-dihydrophenanthrene, 4,5-dihydropyrene, and 5,12-dihydronaphthacene, were employed. The reaction was handled in the absence of air or oxygen at 0°C in 1,2-dichloroethane.

It was observed that the reduction of methylene blue, (Mb) (1.6×10^{-5} mol/l) by di-hydro-aromatic hydrocarbons, (ZH_2) (2.2×10^{-4} mol/l) was a Michaelis-Menten type with respect to the initial concentrations of aromatic hydrocarbons, $(Ar)_0$, in the concentration range from 5.45×10^{-7} to 5.45×10^{-4} mol/l.

The scheme and the rate of the overall reaction may be given as follows:

$$2Mb + Ar \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (Mb_2\cdot Ar)$$

$$(Mb_2\cdot Ar) + ZH_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} (Mb\cdot ZH_2) + Mb + Ar$$

$$(Mb\cdot ZH_2) \xrightarrow{k_3} MbH_2 + Z$$

for $d(Mb\cdot ZH_2)dt=0$ and $k_1,\ k_{-1}\gg k_2$,

$$-d(Mb)/dt = \frac{k_2k_3K(ZH_2)_0(Ar)_0(Mb)^2}{k_3+k_{-2}(Ar)_0(Mb)},$$

which is also equal to $k'(Mb)$, provided that $(Mb)_0\ll(ZH_2)_0$, where $(Mb_2\cdot Ar)$ and $(Mb\cdot ZH_2)$ represent the EDA complex of Mb with Ar and ZH_2 respectively, and where K is equal to k_1/k_{-1}.

Besides such kinetic investigations, new absorption bands were observed in the range between 500 and 600 mμ in the solution of Ar and Mb; for the absorption band of the EDA complex of pyrene and Mb, as a typical example, it was found at 530 mμ. The plots of $(Mb)_0/(O.D.)$ against $1/(Ar)_0^{1/2}(O.D.)^{1/2}$ gave a linear relation according to the Benesi-Hildebrand equation. It is of great interest to note that methylene blue formes EDA complexes with a molar ratio of 2 : 1 with various aromatic hydrocarbons. It was also observed that Mb forms EDA complexes with a molar ratio of 1 : 1 with ZH_2. When ZH_2 was 9,10-dihydroanthracene, the new absorption band was found at 618 mμ.

The reduction of methylene blue by various dihydro-aromatic hydrocarbons was accelerated by a factor of 50 by the formation of the EDA complexes with aromatic hydrocarbons. The rate constant, k', was determined in the initial stage of the reaction when the Z produced from ZH_2 is negligible. The k_1/k_{-1} and k_2/k_{-2} in the above scheme must have some relation with the stabilization energy of the EDA complex formation of Mb with Ar. In fact, the plots of the logarithms of both k_1/k_{-1} and k_2/k_{-2} against the reciprocal of the ionization potential of Ar, a measure of the stabilization energy of the EDA complex formation, gave a good linear relation, as is shown in Fig. 1. This shows that the EDA-complex formation plays a part in the redox reaction.

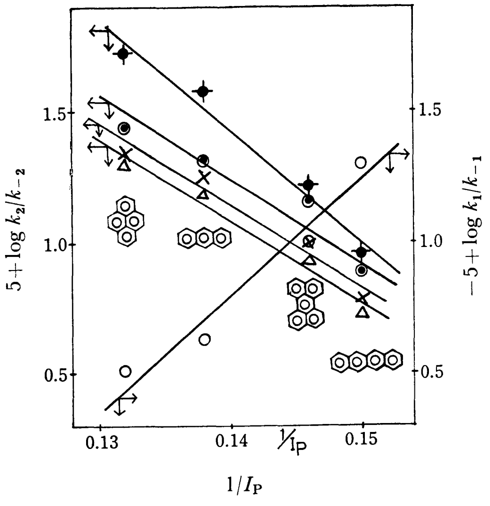

Fig. 1. The ionization potentials of aromatic hydrocarbons and the k_1/k_{-1} in the right scale and the k_2/k_{-2} in the left scale, respectively, in the concentration of aromatic hydrocarbons, 5.45×10^{-4} mol/l: for the k_2/k_{-2}, ✦: 9,10-dihydroanthracene, ⊙: 9,10-dihydrophenanthrene, ×: 5,12-dihydronaphthacene, △: 4,5-dihydropyrene