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Electron Transfer Reaction from Dimethylanilines to Cation Radical of Magnesium Octaethylporphyrin

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A kinetic study of electron transfer reaction from dimethylanilines to cation radical of magnesium octaethylporphyrin reveals that two mechanisms are operating depending on the redox potentials of dimethylanilines.

In photosynthesis, photochemical charge separation producing chlorophyll cation radical is assumed to be the primary process.[1)] Thus far, spectroscopic studies have been made on the nature of cation radical of magnesium porphyrins as a model compound of chlorophyll.[2,3)] For further understanding the role of the cation radical in photosynthesis, it is vitally important to evaluate its reactivity, especially in electron transfer reaction. In this paper, we wish to report a kinetic study of redox reaction involving cation radical of magnesium octaethylporphyrin (MgOEP$^{+\bullet}$Br^{-}; **1**) as an initial approach to chemical elucidation of photosynthesis.

The thermostated methylene chloride solution of **1** (in the concentration range of 5×10^{-8} — 5×10^{-5} M), which was prepared from MgOEP (**2**) by the treatment with bromine,[4)] was quickly mixed with methylene chloride solution of a para-substituted dimethylaniline (**3**a-e) utilizing a stopped-flow apparatus. The reaction was followed with a rapid-scan spectrophotometer (model RA-1300, manufactured by Union Giken Co. Ltd.), monitoring the decrease of the absorption of **1** at 670 nm[4)] and the increase of the absorption of **2** at 408 nm. The reaction temperature was maintained at (17 ± 0.5) °C. In every run, **2** was recovered almost quantitatively on the basis of an electronic spectrum. For para-substituted dimethylanilines (Me$_2$N-Ph-X; **3**d (X=OH) and **3**e (X=NMe$_2$)), the disappearance of **1** followed the simple 2nd-order kinetics as shown in Eq. 1 based on pseudo 1st order treatments concerning **1** and **3**.

$$-d[\mathbf{1}]/dt = k_1[\mathbf{1}][\mathbf{3}] \qquad (1) \qquad\qquad -d[\mathbf{1}]/dt = k_1[\mathbf{1}][\mathbf{3}] + k_2[\mathbf{1}]^2[\mathbf{3}] \qquad (2)$$

Rate constants (k_1) were shown in Table 1. For dimethylanilines (**3**a: X=H, **3**b: X=Me and **3**c: X=OMe), the reaction deviated from Eq. 1 and fitted a more complicated kinetics as shown in Eq. 2, which contained the second and the third-order components. Obtained values of k_1 and k_2 were also shown in Table 1. Both k_1 and k_2 increased on lowering the oxidation potential of **3**.

In Table 1, were also shown one-electron oxidation potentials[6)] of dimethylanilines. The half-wave potential of one-electron oxidation of **2** was reported to be 0.54 V vs. SCE$^{7)}$ which was close to that of **3c**. For electron donors (**3d** and **3e**) with lower potential, **1** oxidized the substrate according to the simple second order kinetics of Eq. 1. On the other hand, when the redox potential of **3** is nearly equal to or higher than that of **2** (i.e., for **3a-c**), the electron transfer reaction proceeded by the mixed mechanism of Eq. 2. The different kinetic profiles may be partly explained on the ground that the contribution of the trimolecular mechanism becomes negligible because of the efficient electron transfer from **3d-e** of low potential. However, there seems to exist some discontinuity in the bimolecular reaction itself, since the plot of logarithms of k_1 versus redox potential (or σ^+ value of the substituents) of **3** did not give a linear free energy relationship but afforded a line like a titration curve whose inflexion point is about 0.5 V. The reason of the unusual behavior of **1** remains to be explored.

It may be worthwhile to note that the trimolecular reaction well competes with the bimolecular one for **3a-c** having higher potential than **2**. This observation is interesting in the point that a multi-photon (i.e., possibly multi-cation-radical) process is involved in photosystem II, where water, a high potential substrate is effectively oxidized.$^{1)}$ The nature of the trimolecular reaction seems to be; 1) a well-known dimer of **1**$^{5)}$ oxidizes **3** and/or 2) the oxidation of **3** with **1** is assisted by another **1** molecule. Further studies are needed for detailed analyses of the electron transfer reaction.

Table 1. Rate constants of the electron transfer reaction from para-substituted dimethylanilines (Me_2N-Ph-X : **3a-e**) to cation radical of MgOEP and one electron oxidation potentials of dimethylanilines.

X	k_1 / $M^{-1}s^{-1}$	k_2 / $M^{-2}s^{-1}$	V vs. SCE$^{6)}$
H : **3a**	8.84 ± 1.44	$(2.21 \pm 0.36) \times 10^6$	0.71
Me : **3b**	$(4.36 \pm 0.50) \times 10$	$(2.18 \pm 0.25) \times 10^7$	0.65
OMe : **3c**	$(2.60 \pm 0.22) \times 10^2$	$(1.30 \pm 0.11) \times 10^8$	0.49
OH : **3d**	$(5.04 \pm 0.45) \times 10^7$		0.30
NMe_2 : **3e**	$> 2 \times 10^8$		0.08

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