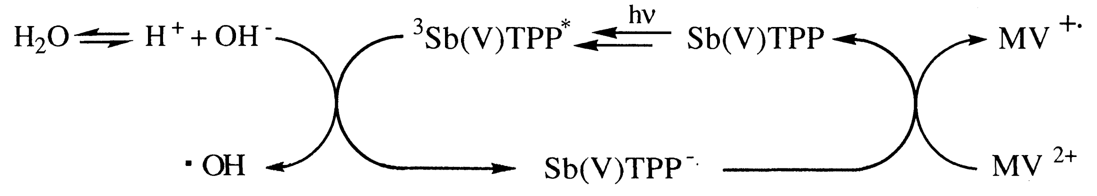
CHEMISTRY LETTERS, pp. 793-796, 1993.

Photochemical Electron Transfer from Hydroxide Ion to the Excited Triplet State of Tetraphenylporphyrinatoantimony(V) upon Visible Light Irradiation in Aqueous Acetonitrile

Shinsuke TAKAGI, Takanobu OKAMOTO, Tsutomu SHIRAGAMI, and Haruo INOUE*
Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University,
1-1 Minamiohsawa, Hachiohji, Tokyo 192-03

Photochemical electron transfer from hydroxide ion to the excited triplet tetraphenylporphyrinatoantimony(V) (Sb(V)TPP) has been found to be induced in aqueous acetonitrile upon visible light irradiation to produce radical anion of Sb(V)TPP as a stable end product.

Many intensive studies have been made on visible light induced photoredox reactions aiming at an artificial photosynthesis such as fixation of carbon dioxide and hydrogen evolution.1) Most of those systems, however, involve sacrificial electron donors in the oxidative terminal end of the redox systems. Attention has thus been focused on how a water molecule as an ideal electron donor could be incorporated in an oxidative terminal end.2) One of the simple candidates for the purpose is an electron transfer from hydroxide ion equilibrated with water in a reaction system. Though several studies have been reported on the electron transfer from OH^- to the excited sensitizer, the light for the excitation has been limited only to an ultra-violet one due to the highly oxidation resistant character of OH^- (E_0=1.9 V vs. NHE in water).3) Since the oxidation potential of OH^- could depend largely on the nature of the solvent,4) one of the crucial factors is the choice of the solvent for the photoredox reaction. Another crucial factor should be the reduction potential of a sensitizer which absorbs light; the more positive is the reduction potential, the less excitation energy is required to induce an electron transfer from OH^- to a sensitizer. In order to induce the electron transfer upon visible light irradiation we chose tetraphenylporphyrinatoantimony(V)($[Sb(V)TPP(OH)_2](OH)$; **1**) as a sensitizer which has a high reduction potential of -0.3 V vs. NHE. We tried to induce the electron transfer in various solvents and have found the first example of visible light induced efficient electron transfer from hydroxide ion in aqueous acetonitrile. When **1** ($2x10^{-6}$M) and potassium hydroxide ($2x10^{-4}$M) in acetonitrile-water mixture(95:5 v/v) was irradiated by



Scheme 1.

visible light (λ=420 nm) under the degassed conditions, the radical anion of **1** was produced with a rather high efficiency; quantum yield was 0.13 under the conditions. Sharp isosbestic points were observed at 406 and 425 nm during the irradiation. The λ_{max}'s (427, 706, 804 nm) in the visible absorption spectrum[5)] and esr measurements (g = 2.000) clearly indicated the formation of the radical anion of **1**. The produced radical anion of **1** was very stable under the conditions and it completely reverted to the starting **1** upon introduction of air after the irradiation. The electron transfer from OH^- would result in a production of hydroxide radical which is known to be a rather strong oxidizing agent. Though the fate of the hydroxide radical is not yet clear, the radical is supposed to abstract a hydrogen atom from the solvent acetonitrile to produce a water molecule, since **1** remained unchanged without suffering an oxidative decomposition even on prolonged irradiation and any decomposition of Rose Bengal (1×10^{-4} M) was not observed at all when the light irradiation to **1** was carried out in the presence of the dye. When methylviologen (MV^{2+})(8×10^{-3}M) was present in the reaction system, its cation radical ($MV^{+\cdot}$) was effectively produced ($\Phi = 0.11$) without any formation of the radical anion of **1**, indicating an electron transfer from the oxidative terminal end (OH^-) equilibrated with water to the reductive terminal one (MV^{2+}) through the sensitizer (**1**) upon visible light irradiation (Scheme 1). The photoredox system could be also coupled with hydrogen evolution system using noble metal such as colloidal platinum or platinum electrode. The photoreduction of **1** into its radical anion was also induced by other electron donors such as 2,5-dimethyl-2,4-hexadiene, 1,4-diphenyl-1,3-butadiene, and triphenylphosphine.

Since fluorescence of **1** was not quenched by OH^- at the concentration in the reaction system, the excited state responsible for the electron transfer should be the excited triplet state of **1**. Oxidation potential of **1** (-0.3 V vs. NHE) and OH^-(1.9 V vs. NHE in water), and the estimated triplet energy (1.8 V)[6)] indicated the electron transfer from OH^- to the excited **1** should be highly endoergic ($\Delta G = 39$ kJ/mol) and very unlikely to occur. Kinetic analyses on double reciprocal plots between the quantum yield of the photoreduction of **1** and the concentration of electron donor afforded the value of intercept/slope which corresponds to the ratio of the rate constants of the electron transfer (kr) against the deactivation of the excited triplet state of **1** (kd). The actual electron transfer from OH^- to the excited **1** in the reaction system was revealed to be faster as compared with the cases of other electron donors which have sufficiently exoergic processes (Table 1). These results strongly

Table 1. Electron Transfer to the Triplet State of **1** in acetonitrile-water mixture(95:5 v/v)

Electron donor	$(kr/kd)^{a)}$/ M	$kr^{b)}$ / $s^{-1}M^{-1}$	$Eox^{c)}$./ V(NHE)	$\Delta G^{d)}$ / kJ mol^{-1}
OH^-	7.7×10^4	3.5×10^9	$1.9^{d)}(0.8^{g)})$	$+39(-68^{h)})$
2,5-Dimethyl-2,4-hexadiene	2.9×10^2	1.3×10^7	$1.5^{e)}$	0
1,4-Diphenyl-1,3-butadiene	5.0×10^3	2.3×10^8	$1.4^{f)}$	-9.6
Triphenylphosphine	1.4×10^4	6.3×10^8	$1.0^{e)}$	-48

a)Intercept/slope estimated in double reciprocal plot between the quantum yield of the photoreduction of **1** and the concentration of electron donor. b)Rate constant of the electron transfer obtained from kr/kd and deactivation rate constant ($kd=4.5\times10^4$ s^{-1}) measured by laser flash photolysis. c)Oxidation potential. d)Free energy change in the electron transfer from electron donor to the excited **1** in its triplet state. e)Peak potential measured by cyclic voltammetry in MeCN. f)Ref. 7. g)Ref. 4. h)Calculated value from Eox(OH^-) = 0.8 V.

suggest that the actual oxidation potential of OH^- in aqueous acetonitrile has a much lower value than the estimated one in water. The oxidation potential of OH^- in pure acetonitrile has not been determined experimentally but been postulated to be shifted to around 0.8 V vs. NHE on the basis of several hypotheses on solvation energy of ionic species.[4)] Supposing the value of 0.8 V vs. NHE, the electron transfer would be exoergic process (ΔG = -68 kJ/mol) in acetonitrile. In fact, very interestingly, the reactivity of the electron transfer from OH^- to the excited **1** was very much affected by the amount of water in acetonitrile; the quantum yield increased sharply below 18% (v/v) content of water, while almost no reaction occurred in water (Fig. 1). The results could be explained by supposing the oxidation potential of OH^- decreasing with decrease of water content in acetonitrile. The present study is one of the typical examples in accord with the Eberson's prediction on the shift of the oxidation potential of OH^- in organic solvents.

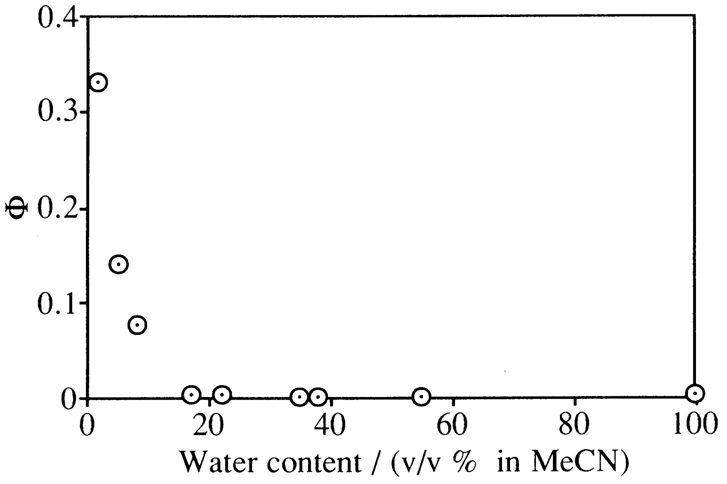


Fig. 1. Quantum yield of electron transfer from hydroxide ion to the excited triplet Sb(V)TPP in aqueous acetonitrile; [**1**] = 2×10^{-6} M, [OH^-] = 1×10^{-3} M.

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture and the Special Research Project of Tokyo Metropolitan University.

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5)One electron reductive electrolysis of **1** at -0.3 V vs. NHE in acetonitrile containing tetrabutylammonium perchlorate as a supporting electrolyte afforded the radical anion of **1** (λmax; 427, 706, 804 nm).

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(Received January 21, 1993)