

ARTIFICIAL PHOTOSYNTHESIS. MECHANISM AND APPLICATION

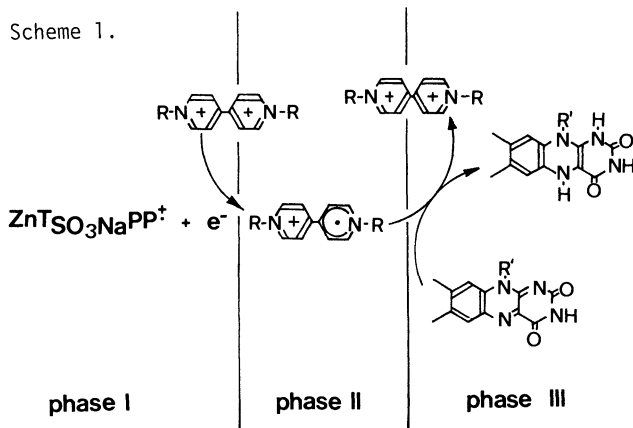
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Abstract — An artificial photosynthesis system may be prepared by ideal "coupling" of elemental chemical processes. The ideal "coupling" is basically achieved by the detailed kinetic "balance" of elemental processes and the rate or equilibrium of every elemental process is very sensitive to a slight change in structure of the component, concentrations, pH and intensity of irradiated light. Two artificial "total" systems were prepared; for a bacteria photosynthesis model and for a completely artificial H₂ generation system.

Chemistry of photosynthesis may be well understood as a successful combination of several chemical events — (i) photon absorption, (ii) energy transfer, (iii) charge-separation, (iv) electron-transport, (v) chemical reactions at the oxidation and reduction ends, and (vi) chemical reactions coupled with electron-transport. Every chemical event seems simple to understand and yet difficult to "mimic". Major problem remained unsolved in the chemistry of photosynthesis is, therefore, possible mechanism of the successful combination of every elemental chemical process.

One of the ideal tools to combine a charge separation and electron fixation process (reduction end), for example, is a membrane modified with an extremely efficient electron transporting compound in the presence of a remarkable oxidation-reduction potential difference across the membrane. Thus, from the charge separated pair formed by the irradiation of the reaction center model electron is efficiently transported to the "reduction end". This situation is schematically depicted in Scheme 1 (Ref. 1 & 2).



This facile electron transport considerably reduces the so-called "back reaction" rate of the charge separation species, increasing quantum yield of artificial photosynthesis markedly. In this way, some of elemental chemical processes are combined to produce a system of "higher function".

It is concluded, therefore, that efficiency of the combination of two (or more) elemental chemical processes is extremely important. And the efficiency of the combination is mostly determined by the rate constants of elemental processes and the concentrations of components. Some typical

examples of the significant effect of the small structure change in the component on the rate constant of an elemental process and equilibrium constant are shown in the Tables below.

Distribution of Viologen Dications

Viologen dications	CH ₂ Cl ₂ %	H ₂ O ^a %
MeV ²⁺	0	100
C ₆ V ²⁺	0	100
C ₈ V ²⁺	1	99
C ₁₂ V ²⁺	19	81
C ₁₂ Py ⁺ Py ⁺ CH ₂ CO ₂ ⁻	2	98

^a pH 6.8, 25°C.

Distribution of Viologen Cation Radicals

Viologen cation radicals	CH ₂ Cl ₂ %	H ₂ O ^a %
MeV ^{•+}	7	93
C ₃ V ^{•+}	21	79
C ₅ V ^{•+}	71	29
C ₆ V ^{•+}	88	12
C ₈ V ^{•+}	95	5
C ₁₂ N ⁺ Py ⁺ CH ₂ CO ₂ ⁻	10	90

^a pH 6.8, 25°C.

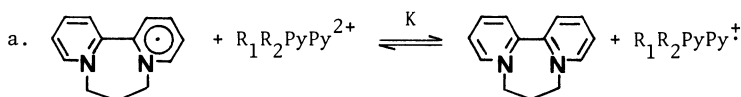
Oxidation of Viologen Cation Radicals with FMN
in the Presence of CTAB

Viologen cation radicals	FMN	k ₂ × 10 ³ mol ⁻¹ ·s ⁻¹
MeV ^{•+} 7.0 × 10 ⁻⁵ M	1.0 × 10 ⁻⁴ M	59
C ₃ V ^{•+} 1.5 × 10 ⁻⁵	1.4 × 10 ⁻⁴	13
C ₅ V ^{•+} 1.0 × 10 ⁻⁴	1.6 × 10 ⁻⁴	8.2
C ₆ V ^{•+} 4.5 × 10 ⁻⁵	1.4 × 10 ⁻⁴	6.8
C ₈ V ^{•+} 5.7 × 10 ⁻⁵	9.4 × 10 ⁻⁵	4.0
C ₁₂ Py ⁺ Py ⁺ CH ₂ CO ₂ ⁻ 5.0 × 10 ⁻⁵	1.0 × 10 ⁻⁴	1.3

25°C, pH 6.8, [CTAB] = 2.0 × 10⁻² M, [Micelle] = 3.2 × 10⁻⁴ M.

Interconversion Between Bipyridyl Cation Radicals.
Equilibrium Constants and Reduction Potentials
(pH 4.5, in 0.1 M oxalate).

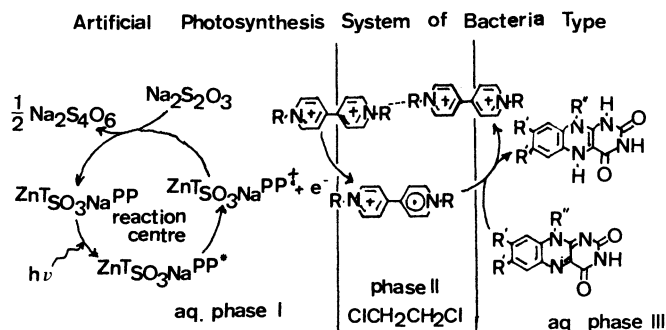
Radical cation	Equilibrium const. ^a	Reduction potential
	1 (standard)	-0.105 ± 0.001
CH ₃ -N ⁺	60 ± 2	(standard)
CH ₃ -N ⁺	4.5 ± 0.3	-0.067 ± 0.003
nC ₆ H ₁₃ -N ⁺	5.4 ± 0.5	-0.062 ± 0.006
H-N ⁺	1.1 ± 0.1	-0.102 ± 0.002



b. Taking methylviologen (-0.44 V vs NHE)^{1d} as a standard.

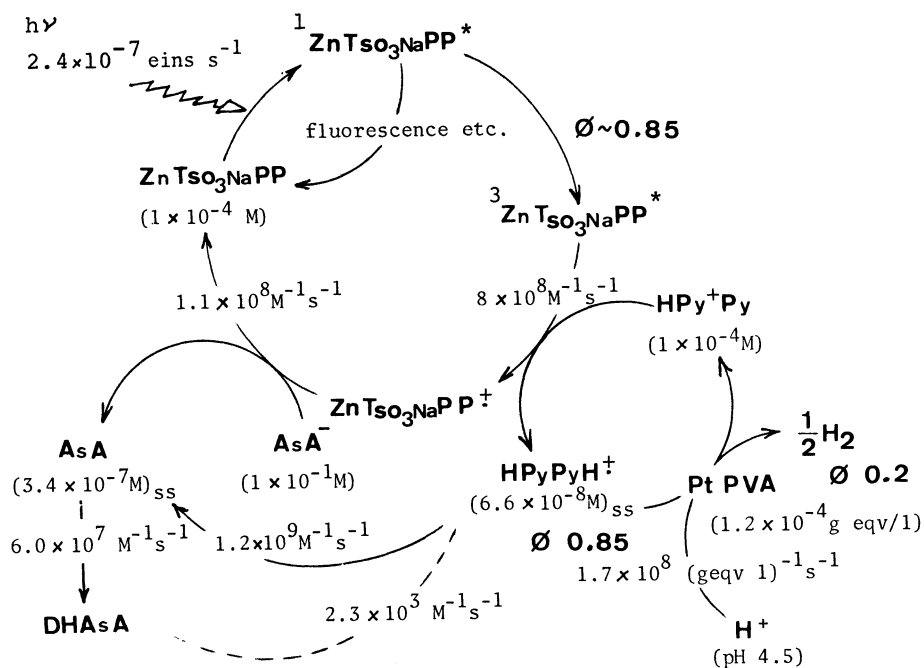
Through the detailed study of every elemental rate process the "conditions" for ideal combination of a pair of elemental processes is determined. This kind of molecular design gives an artificial photosynthesis system of satisfactorily high quantum yield. Thus, bacteria photosynthesis model was successfully prepared;

Scheme 2.



This kind of molecular design based on the optimization of the steady state rate may be further applied to a variety of multi-process reactions. An artificial hydrogen generation system of high quantum yield was similarly designed;

Scheme 3.



It is concluded that the overall quantum yield is very sensitive to the slight change in experimental conditions such as concentrations of components, wave length and intensity of irradiated light or pH of the medium. It is because of the very delicate balance of elemental rate processes involved.

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