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SPLITTING OF WATER INTO HYDROGEN AND HYDROGEN PEROXIDE BY LIGHT IRRADIATION OF ANTHRAQUINONE DERIVATIVES

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Water splitting into hydrogen and hydrogen peroxide system is developed which contains anthraquinone as a photosensitizer, methyl viologen as an electron transfer agent and colloidal platinum as a catalyst.

Photoinduced splitting of water into hydrogen and hydrogen peroxide, or hydrogen and oxygen with light absorbing species has been studied[1,2] as a means of solar energy storage, and the research being carried out focuses on the development of an efficient system capable of water splitting.

Anthraquinone derivatives are well-known photosensitizers[3] and can be reduced in alkaline alcoholic solution, and the production of the corresponding semiquinone anion radical have been established as a result of electron transfer from hydroxyl ions[4-6].

By adding methyl viologen to the system, we found the formation of cation radical (MV^+) of methyl viologen. As MV^+ is known to produce hydrogen in the presence of a suitable catalyst, an attempt was made to reduce water to hydrogen by the use of a modified system which combines a photosensitizer, methyl viologen photoirradiation system and a catalyst such as colloidal platinum.

All reagents were obtained from commercial sources and were of the highest purity available. Sodium-9,10-anthraquinone-2,6-disulfonate (I) and sodium-9,10-anthraquinone-2-sulfonate (II) were used as photosensitizers. A typical experiment was performed as follows under anaerobic conditions at 30°C. A reaction mixture containing 1.0×10^{-4} M of photosensitizer, 3.6×10^{-3} M of sodium hydroxide and 3.52×10^{-4} M of methyl viologen in 6 ml of ethanolic aqueous solution ($C_2H_5OH : H_2O = 1 : 1$ v/v) was irradiated by 200 W tungsten lamp. The light of wavelength less than 350 nm was cut off by a Toshiba UV-D35 filter. Colloidal platinum was prepared according to the literature[7].

When the alkaline alcoholic solution containing (I) was irradiated, the semiquinone anion radical (AQ^-), which has characteristic bands at 405 and 523 nm, was formed. The AQ^- formation was also confirmed by ESR measurements. The AQ^- concentration increases after an induction period with irradiation time and reaches a constant value as shown in the figure, curve a. In the presence of methyl viologen no AQ^- was detected, but the growth of MV^+ was observed as shown by curve b. The rate decrease may be caused by the decrease of the reactant concentration. When methyl viologen was added to the solution containing (I) after 10 min

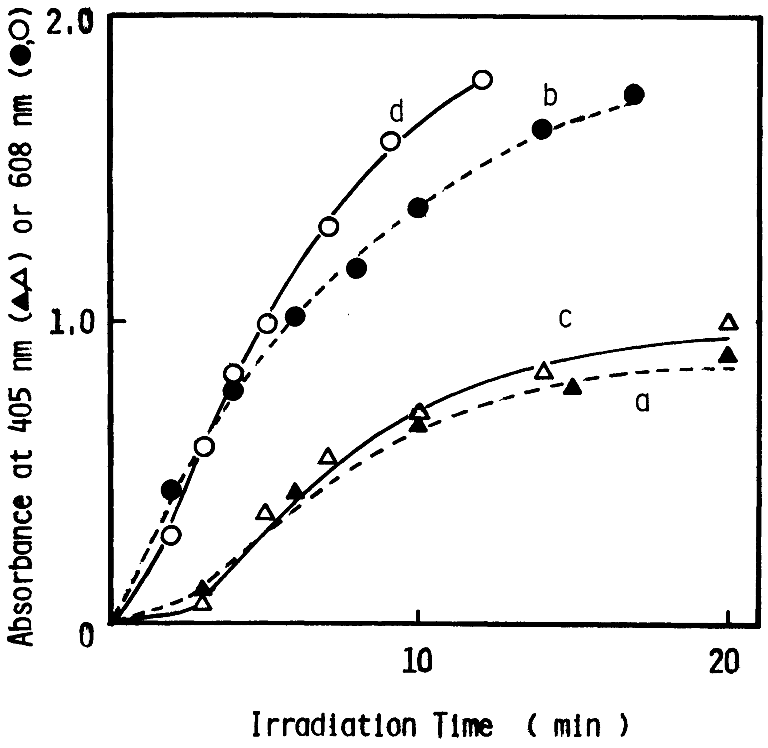
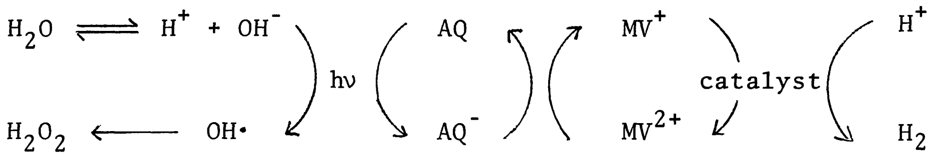


Figure: Time dependence of absorbance at 405 nm due to AQ^- and at 608 nm due to MV^+.
▲: compound I, △: compound II, ●: compound I + methyl viologen, ○: compound II + methyl viologen. See text for reaction conditions.

irradiation, AQ^- disappeared immediately and MV^+ appeared in place of AQ^-. The formation of hydrogen peroxide was detected by polarographic analysis after 30 min irradiation of the anthraquinone solution or methyl viologen containing system. As shown in the figure, curve c and d, similar results were obtained in the case of the system containing (II) as a photosensitizer. The above results strongly indicate that an electron transfers from hydroxyl ion to methyl viologen through the photoexcited state of anthraquinone.

When 9.95×10^{-5} M of colloidal platinum was added in the system containing (I) or (II) (3.33×10^{-4} M), methyl viologen (7.8×10^{-4} M) and NaOH (2.52×10^{-3} M), 0.13μmol of hydrogen evolution was observed in both cases after 40 h irradiation. Hydrogen evolution was also observed by the irradiation of sunlight instead of a tungsten lamp.

From the above results, the following mechanism is proposed for the splitting of water into hydrogen and hydrogen peroxide by the irradiation of anthraquinone.



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