

Preliminary Note

Photoinduced hydrogen evolution from alcohols catalysed by benzophenone and colloidal platinum

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Photooxidation of alcohols in the presence of benzophenone has been studied extensively under irradiation with near-UV light [1 - 4]. When methyl viologen (1,1'-dimethyl-4,4'-bipyridinium chloride) is added to an alcohol-benzophenone system, reduction of the methyl viologen has been observed [5]. As the reduced form of methyl viologen has a sufficiently high redox potential to produce hydrogen from water, an attempt to obtain hydrogen was made using a system which combines photoirradiation and a catalyst.

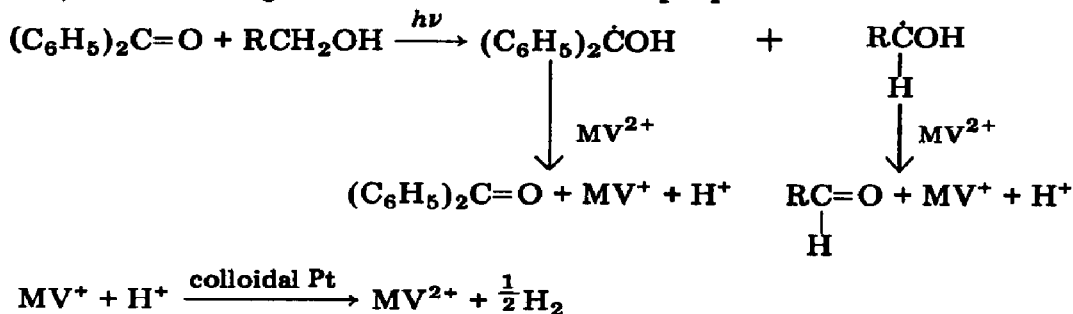
All reagents were obtained from commercial sources and were of the highest purity available. Colloidal platinum was prepared according to the method described previously [6].

The reaction mixture contained 1.74×10^{-4} mol of benzophenone and 5.58×10^{-7} mol of colloidal platinum in a 1:1 ethanol-water solution or a 1:1 2-propanol-water solution. For a methanol-water solution the ratio of methanol to water was 1.5:1 in accordance with the solubility of benzophenone in methanol.

The sample (5 ml) in a Pyrex reactor was then irradiated with light of wavelengths exceeding 320 nm (150 W tungsten lamp) under anaerobic conditions at 30 °C. The hydrogen evolved was analysed using gas chromatography. With the use of UV-35 and UV-39 Toshiba filters the effective wavelength range was limited to 350 - 390 nm.

Although benzophenone was converted into benzpinacol by near-UV light irradiation of a 2-propanol-benzophenone solution, the benzophenone remained unchanged when methyl viologen was added to the system (Fig. 1) and benzpinacol was not detected. Similar phenomena were observed for other alcohols, such as methanol or ethanol, and formaldehyde, acetaldehyde or acetone were detected in the respective systems. Methyl viologen was reduced in all systems and the concentration of the reduced form of methyl viologen increased with irradiation time.

Hydrogen was evolved as a result of alcohol dehydrogenation on the addition of colloidal platinum to the methyl viologen–benzophenone–alcohol photoirradiation system as shown in Fig. 2. Since benzophenone serves as a photosensitizer and colloidal platinum serves as a catalyst in these systems, the following reaction mechanism was proposed:



where MV^{2+} and MV^+ are the oxidized and reduced forms of methyl viologen respectively.

The direct irradiation of the system by sunlight was also investigated. Because sunlight contains some UV radiation, it promotes an efficient conversion to hydrogen. Since the formation of aldehyde and hydrogen from alcohol is an endothermic reaction, these systems may be able to store solar energy as chemical energy. This work is now in progress.

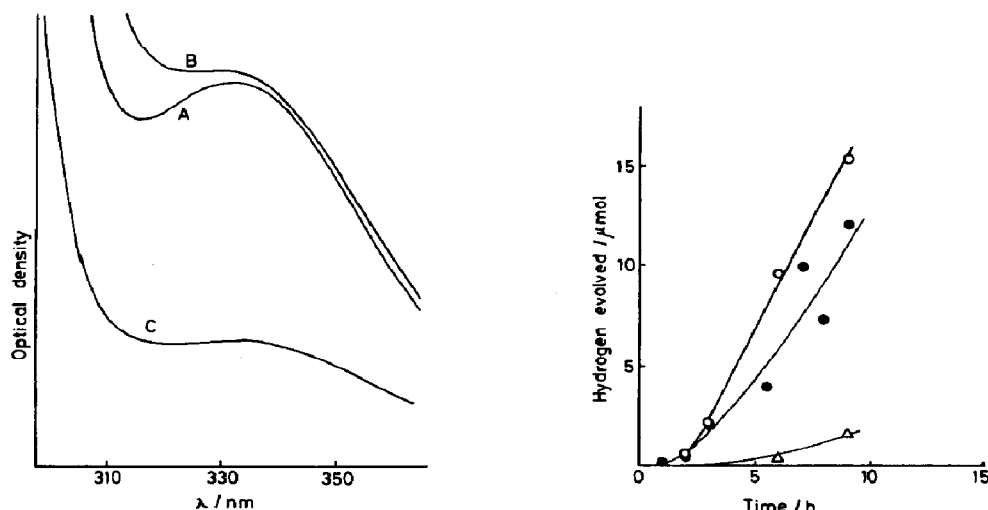


Fig. 1. The effect of methyl viologen on the electronic spectra: A, electronic spectrum of a solution containing benzophenone (8.7×10^{-5} mol) in 5 ml of a 2-propanol–water solution; B, solution A after addition of methyl viologen (4.0×10^{-2} mol) and irradiation for 3 h; C, solution A after irradiation for 3 h.

Fig. 2. The time dependence of hydrogen evolution in benzophenone–alcohol–methyl viologen–colloidal platinum systems: O, 2-propanol; ●, ethanol; Δ, methanol (see text for reaction conditions).

Acknowledgment

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