



Photochemical and enzymatic methanol synthesis from HCO_3^- by dehydrogenases using water-soluble zinc porphyrin in aqueous media

Yutaka Amao*, Tomoe Watanabe

Department of Applied Chemistry, Oita University, Dannoharu 700, Oita 870-1192, Japan

ARTICLE INFO

Article history:

Received 23 May 2008

Received in revised form 13 August 2008

Accepted 13 August 2008

Available online 22 August 2008

Keywords:

CO_2 fixation

Methanol synthesis

Artificial photosynthesis

Biocatalysis

Photochemical reaction

ABSTRACT

We studied the photochemical and enzymatic synthesis of methanol from HCO_3^- using formate dehydrogenase (FDH) isolated from *Candida boidinii*, aldehyde dehydrogenase (AldDH) and alcohol dehydrogenase (ADH) isolated from yeast, and the photoreduction of methyl viologen (MV^{2+}) by the visible-light sensitization using zinc tetraphenylporphyrin tetrasulfonate (ZnTPPS) in the presence of triethanolamine (TEOA). When a sample solution containing ZnTPPS, MV^{2+} , FDH, AldDH, ADH, TEOA, and NaHCO_3 in potassium phosphate buffer solution (pH 8) was irradiated, the amount of methanol produced increased with the irradiation time. After irradiation for 3 h, $4.5 \mu\text{mol dm}^{-3}$ of methanol was produced from $100 \mu\text{mol dm}^{-3}$ NaHCO_3 . The conversion ratio of HCO_3^- to methanol was approximately 4.5%. This result indicates that a system for the photochemical synthesis of methanol from HCO_3^- can be developed by using three dehydrogenases (FDH, AldDH, and ADH) and for the photoreduction of MV^{2+} through the photosensitization of ZnTPPS in aqueous media.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The fixation and utilization of CO_2 are potential steps for realizing the catalytic reduction of CO_2 [1–3]. Many researchers have attempted the electrocatalyzed reduction of CO_2 using specific electrode materials [4]. Further, in studies on CO_2 fixation, researchers have also investigated photocatalysis on titanium dioxide, silicon carbide, and strontium titanate surfaces [5,6]. However, these systems use ultraviolet irradiation and give very poor yields; hence, a highly efficient CO_2 fixation system that uses visible-light is desired.

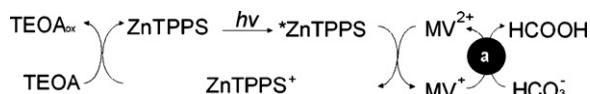
Visible-light-induced photoredox systems that consist of an electron donor, a photosensitizer, and an electron relay have been widely studied [7]. An effective photosensitizer is an essential component of such systems. Ruthenium(II) coordination compounds and porphyrins are widely used as effective photosensitizers in photoredox systems. Water-soluble zinc porphyrins such as zinc tetraphenylporphyrin tetrasulfonate (ZnTPPS) and zinc tetrakis (4-methylpyridyl) porphyrin (ZnTMPyP) exhibit strong absorption bands in the visible region (380–600 nm); hence, they are more widely used as photosensitizers than ruthenium(II) coordination compounds [8–11]. Further, biological and enzymatic CO_2 fixation systems have also received considerable attention. For

example, CO_2 can be reduced to formic acid by using formate dehydrogenase (FDH) and nicotinamide adenine dinucleotide dehydrogenase (NADH) [12]. Therefore, a homogeneous photochemical CO_2 reduction system that combines the photoreduction of NAD^+ through the photosensitization of water-soluble zinc porphyrin and ferredoxin- NADP^+ reductase (FDR) and the reduction of CO_2 using FDH is established.

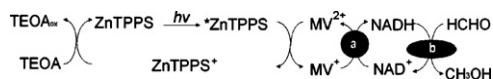
Some examples related to the photochemical CO_2 reduction with enzymes have been reported. A CO_2 fixation system based on malic acid synthesis from pyruvate and HCO_3^- with malic enzyme combined with the photoreduction of NAD^+ by the photosensitization of chemically modified chlorophyll and FDR has also been reported [13]. The enzymatic synthesis of formic acid from HCO_3^- with FDH and the photoreduction of MV^{2+} using a system containing a ruthenium(II) coordination compound as a photosensitizer and mercaptoethanol as an electron donor has also been reported [14]. We have previously reported the visible-light-induced enzymatic synthesis of formic acid from HCO_3^- with FDH through the photosensitization of water-soluble zinc porphyrins, ZnTPPS or ZnTMPyP, in the presence of triethanolamine (TEOA) as an electron donor, as shown in Scheme 1 [15–17]. We have also reported a system for visible-light-induced methanol synthesis from formaldehyde using ADH isolated from *Saccharomyces cerevisiae* and NAD^+ photoreduction through the visible-light photosensitization of ZnTPPS in the presence of TEOA, as shown in Scheme 2 [18,19]. In this system, $0.38 \mu\text{mol dm}^{-3}$ of methanol is produced from $16 \mu\text{mol dm}^{-3}$ of formaldehyde after irradiation

* Corresponding author. Tel.: +81 97 554 7972; fax: +81 97 554 7972.

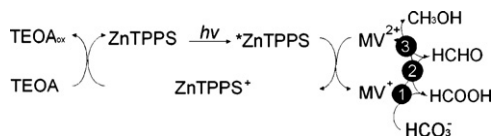
E-mail address: amao@cc.oita-u.ac.jp (Y. Amao).



Scheme 1. Photochemical and enzymatic formic acid synthesis from HCO_3^- with FDH (a) and photoreduction of MV^{2+} with TEOA and ZnTPPS.



Scheme 2. Photochemical methanol synthesis from formaldehyde with alcohol dehydrogenase (ADH; b) via the photoreduction of NAD^+ with diaphorase (a) using ZnTPPS photosensitization.



Scheme 3. Photochemical and enzymatic methanol synthesis from HCO_3^- with formate (1), aldehyde (2), and alcohol dehydrogenases (3) via the photoreduction of MV^{2+} using ZnTPPS photosensitization.

for 180 min. The conversion ratio of formaldehyde to methanol is approximately 2.3%. However, as shown in Scheme 2, the use of two electronic carrier molecules, methyl viologen and NAD^+ , and the enzyme diaphorase complicates the reaction system. Since the NADH formed plays the same role as TEOA, the production efficiency of methanol will be lowered. Therefore, we propose the use of methyl viologen as the electron carrier and a dehydrogenase substrate. The photochemical synthesis of methanol from the HCO_3^- system, as shown in Scheme 3, is accomplished by adding aldehyde dehydrogenase (AldDH) and alcohol dehydrogenase (ADH) in the above-mentioned visible-light-induced formic acid synthesis system by the combination of Schemes 1 and 2. Although reactions shown in Schemes 1 and 2 that use each dehydrogenase, FDH and AldDH have been successfully carried out, the development of a methanol synthesis system using all the three dehydrogenases (FDH, ADH, AldDH), as shown in Scheme 3 is difficult, since it requires optimization of enzyme activity and stabilization of the intermediate, especially formaldehyde. Thus, considerable efforts have gone into the development of the methanol synthesis system shown in Scheme 3. Yoneyama and coworkers reported the electrocatalytic synthesis of methanol from a CO_2 -saturated buffer solution using FDH and ADH [20]. We have previously reported in a communication letter, the development of photochemical and enzymatic methanol synthesis from HCO_3^- using FDH, AldDH, and ADH via the photoreduction of methyl viologen (MV^{2+}) using ZnTPPS photosensitization [21]. However, the mechanism of this reaction has not yet been clarified.

In this paper, we describe a system for visible-light-induced methanol synthesis from HCO_3^- by using FDH, AldDH, and ADH, and MV^{2+} photoreduction through the visible-light photosensitization of ZnTPPS in the presence of TEOA as an electron donor in an aqueous medium.

2. Experimental

2.1. Materials

FDH from *Candida boidinii* and AldDH from yeast were obtained from Roche Co., Ltd. ADH from yeast was purchased from Oriental Yeast Co., Ltd. Tetraphenylporphyrin tetrasulfonate (H_2TPPS) was purchased from Tokyo Chemical Industry Co., Ltd. Other chemicals were of analytical grade or of the highest grade available.

2.2. Synthesis of ZnTPPS

ZnTPPS was synthesized by refluxing H_2TPPS with approximately 10 times molar equivalent of zinc acetate in 100 ml methanol at 40°C for 2 h. The insertion of the zinc ion into H_2TPPS was monitored by visible absorption spectroscopy. During the reaction, the intensity of the characteristic absorption band of ZnTPPS at 550 nm increased, while that of the absorption band due to H_2TPPS at 650 nm decreased gradually. After evaporation of the solvent, the product was dissolved in distilled water and used as such for the subsequent experiments. Although the excess zinc acetate was not removed from the ZnTPPS solution, it has been confirmed that zinc acetate has no influence on the subsequent photoreactions [22].

2.3. Enzyme activity

One unit of FDH activity was defined as the amount of enzyme required to convert $1.0\ \mu\text{mol}$ formic acid to NaHCO_3 in 1 min in the presence of NAD^+ . One unit of AldDH activity was defined as the amount of enzyme required to convert $1.0\ \mu\text{mol}$ formaldehyde to formic acid in 1 min in the presence of NAD^+ . One unit of ADH activity was defined as the amount of enzyme required to convert $1.0\ \mu\text{mol}$ methanol to formaldehyde in 1 min in the presence of NAD^+ .

2.4. Photoreduction of MV^{2+}

A solution containing ZnTPPS ($0.1\ \mu\text{mol dm}^{-3}$), MV^{2+} , and TEOA ($0.3\ \text{mol dm}^{-3}$) in 3.0 ml of $10\ \text{mmol dm}^{-3}$ potassium phosphate buffer (pH 8) was deaerated by six freeze–pump–thaw cycles. The sample solution was irradiated at 30°C by a 200-W tungsten lamp (Philips) placed at a distance of 3.0 cm from the sample; this tungsten lamp was equipped with a Toshiba L-39 cut-off filter. The MV^+ concentration was determined from the absorbance at 605 nm at a molar extinction coefficient of $13,000\ \text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1}$ [23].

2.5. Enzymatic and photochemical methanol production

A sample solution containing ZnTPPS ($0.1\ \mu\text{mol dm}^{-3}$), MV^{2+} ($0.1\ \text{mmol dm}^{-3}$), TEOA ($0.3\ \text{mol dm}^{-3}$), FDH, AldDH (12.5 units), and ADH (12.5 units) was deaerated by six freeze–pump–thaw cycles and then by flushing with argon gas for 5 min. The sample solution was irradiated after the addition of NaHCO_3 . The amount of methanol produced was measured by gas chromatography (GC) using a 25% Sorbitol-Gasport B column (i.d.: $2\ \text{m} \times 3\ \text{mm}$; GL Sciences) attached to a Shimadzu GC-8A gas chromatograph (oven temperature: 100°C ; carrier gas: N_2 ; flow rate: $21.8\ \text{ml min}^{-1}$). The by-products formed in the reaction were analyzed by high-pressure liquid chromatography (HPLC) with an electrical conductivity detector (Shimadzu CDD-10A_{VP}) (column temperature: 40°C ; column: polystyrene sulfonate column, Shimadzu SCR-H; elutant: *p*-toluene sulfonic acid; flow rate: $0.8\ \text{ml min}^{-1}$).

3. Results and discussion

3.1. Photoreduction of MV^{2+}

The photoreduction of MV^{2+} is the most important step in photochemical synthesis of methanol from the HCO_3^- system. The reaction conditions required for obtaining the highest yield of the reduction product MV^+ were investigated. The time dependence of the MV^+ concentration in the system containing ZnTPPS, MV^{2+} , and TEOA for various MV^{2+} concentrations under visible-light irradiation

Download English Version:

<https://daneshyari.com/en/article/47869>

Download Persian Version:

<https://daneshyari.com/article/47869>

[Daneshyari.com](https://daneshyari.com)