Monoalkyl viologens are effective carbohydrate O_2-oxidation catalysts for electrical energy generation by fuel cells

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ABSTRACT

Dialkyl viologens are known to be effective catalysts for carbohydrate oxidation by O_2 under the mild conditions of room temperature and pH 9–12 and have been used to construct a simple carbohydrate fuel cell. The mechanism of carbohydrate oxidation proceeds by a stepwise, dialkyl viologen-mediated, sequential oxidation starting at the anomeric carbon and continuing down the carbohydrate chain producing carbonate and formate as products without loss of dialkyl viologen catalytic function. At pH values >13 the dialkyl viologens undergo a complex hydrolysis reaction forming monoalkyl viologen. The hydrolysis mixture catalytically oxidizes carbohydrate and monoalkyl viologen was confirmed as the active catalysts using independently synthesized monoalkyl viologens. Monoalkyl viologens are stable and catalytically active toward carbohydrate oxidation from pH 9.0 to conditions of 3.0 M KOH. Mono-alkyl viologens react at a rate approximately 50% of that of dialkyl viologens, but are more stable at high pH, making them versatile carbohydrate oxidation catalysts for fuel cell use. Because of a more negative redox potential, monoalkyl viologens more efficiently convert the chemical energy of carbohydrates into electrical energy. The catalytic reactivity of monoalkyl viologens reported here should be of use as homogeneous and immobilized catalysts in alkaline carbohydrate fuel cells.

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1. Introduction

Carbohydrates are abundant, high-energy biomolecules whose stored chemical energy is released through complex enzymatic cycles to meet the varied energy requirements of the diverse living organisms on earth [1]. The versatility and high-energy content of glucose, carbohydrates in general, and certain related molecules suggest they can be used to produce liquid fuels [2–5] and even for the direct production of electricity from biomass [6–10]. Although this latter possibility has been investigated for the last half century [11], little progress using carbohydrates as a source for electrical power has been made. This is because carbohydrates are inherently resistant to complete O_2-oxidation and efficient and inexpensive catalytic systems have not been developed to catalyze this reaction.

Recent reports now have established that carbohydrates can be catalytically oxidized by O_2 at high efficiency at mildly acidic [12] and mildly alkaline conditions [13–15] using vanadium and dialkyl viologen catalysts, respectively. The viologen catalytic process was subsequently developed to produce a fuel cell giving a current

density of 30 mA/cm^2 [13,15]. Two different sets of conditions were reported for viologen-catalyzed carbohydrate fuel cell operation. The first [13,14] occurs at pH of 9–12 and the second [15], occurs at the more basic conditions of 1.0–3.0 M KOH.

Viologen-catalyzed carbohydrate oxidation under the milder pH conditions has now been extensively investigated [14], and the results show two possible carbohydrate oxidation pathways. One is a minor, nonspecific oxidation of carbohydrates by O_2 with no net production of electrical current and a second is the specific, viol-ogen-catalyzed oxidation of carbohydrates, which generates useful electrical energy in a fuel cell. When the enediol form of the carbohydrate reacts directly with O_2 by the first process, a carbox-ylic acid (i.e. gluconic acid from glucose) is typically formed [17]. Once formed, acids are not further oxidized and carbohydrate oxidation terminates. The second and more important pathway occurs when the enediol form is rapidly oxidized by the viologen catalyst forming reduced viologen. O_2 or a fuel cell electrode then oxidizes the viologen catalyst completing carbohydrate oxidation. A catalytic cycle is formed in which carbohydrate oxidation is mediated by the viologen catalyst.

The mechanism for this pathway consists of the stepwise oxidation of the open chain form of the carbohydrate to release carbonate and some formate, with formation of the next

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carbohydrate, which is one carbon atom shorter. This process continues until the carbohydrate is completely oxidized to carbonate and formate. However, even when the specific viologen-catalyzed pathway is functioning, carboxylic acids and other unreactive products inadvertently form to small but varying degrees [16], terminating further reaction and decreasing the overall efficiency of carbohydrate oxidation. High viologen/carbohydrate ratios minimized formation of these unreactive intermediates and highly efficient carbohydrate oxidation (~80%) by O_2 was reported [13,14].

In order to extend our previous studies at pH 9–12 to more basic conditions where a greater production of electrical energy occurs from carbohydrate oxidation, we examined carbohydrate oxidation in 1–3 M KOH. The results established that dialkyl viologens are initially catalytically active but are inherently unstable in strong base and undergo hydrolysis to release one alkyl group. The released alkyl group acts as reductant for the remaining viologens or is oxidized by O_2. Monoalkyl viologens were produced in high yield during hydrolysis and were also found to be effective carbohydrate oxidation catalysts. Here, we report the catalytic properties of the resulting monoalkyl viologens as catalysts for carbohydrate oxidation and also describe the hydrolysis reaction of dialkyl viologens in strong base.

2. Materials and methods

2.1. Materials

Saturated KOH solutions (~19.6 M), in which K_2CO_3 is not soluble, were used to prepare carbonate-free 1.0–3.0 M KOH solutions for viologen-catalyzed carbohydrate oxidation reactions. Specifically labeled ^{13}C glyceraldehyde (98 atom%, Omicron Biochemicals, Inc. South Bend, IN) and glucose (99 atom%, Sigma, St. Louis, MO) were used to identify carbohydrate oxidation products by ^{13}C NMR (Inova 300).

MV (methyl viologen) and EV (ethyl viologen) are the dimethyl and diethyl 1,1′-dialkyl-4,4′-bipyridine derivatives used as their dichloride or dibromide salts, respectively, and were obtained from Sigma. For MV the chemical reduction reaction is: $MV^{2+} + e = MV^{1+}$. MMV and MEV are the N-1-alkyl-4, 4′-bipyridine derivatives used as their iodide salts. MMV and MEV, and other monoalkyl viologens, were synthesized by adding bipyridine and the appropriate iodoalkane to acetone in a 1:1 ratio and refluxing overnight. The monoalkyl iodide salts precipitate as high purity products. For MMV the chemical reduction reaction is: $MMV^{1+} + e = MMV^0$.

2.2. Methods

NMR and mass spectrometry (MS, Agilent Technologies LC/MS TOF) were used to identify viologen species. Pressure-cell measurements and vial measurements were used to measure O_2-uptake [13,14]. Microcoulometry was conducted anaerobically [20] in a coulometry cell containing viologen and buffer that was set at −400 mV relative to the saturated calomel electrode. As the viologen catalyst oxidizes the carbohydrate and forms reduced viologen, the latter is oxidized at the silver electrode and the resulting oxidation current is integrated over time to obtain the total coulombs transferred during carbohydrate oxidation.

2.3. Fuel cell

The fuel cell (Fig. 4) was a modified direct-methanol fuel cell that is commercially available (fuelcellstore.com, SKU 1071041, Boulder, CO) and its use is previously described [13]. The anode

plate is stainless steel and the current collector is a 2.5 cm^2 piece of the nickel foam (Marketech International, USA). The cathode material was the E-4 air cathode purchased at electric-fuel.com. A Teflon-coated stir bar anchored on a wire was used to stir the homogeneous anaerobic solution of buffer, carbohydrate and dialkyl and monoalkyl viologens. The fuel-containing chamber at the anode was closed to mass flow and was used to compare the current flow for catalyzed reactions using MV vs. MMV. The viologen, fuel, and buffered electrolyte were added to a 7-mL chamber (seen as the 'catalyst + fuel' area in Fig. 4) and the generated current was collected using a Gamry PC4/750 Potentiostat. A gluconic acid and MV control was run to demonstrate that gluconic acid does not react with MV, nor is the gluconic acid spontaneously oxidized in 3 M KOH. This non-reactivity of gluconic acid indicates that current flow must be due to the viologen oxidation carbohydrate pathway.

3. Results

3.1. Viologen-catalyzed carbohydrate oxidation

The addition of MV (or other dialkyl viologens) and glyceraldehyde to strong base (1.0–3.0 M KOH) rapidly turns dark blue, indicating that MV has oxidized glyceraldehyde with formation of reduced MV. Fig. 1 shows the pressure change (O_2-uptake) as reduced MV is oxidized by air in 1.0 M KOH. Similar reactions occur for glucose and dihydroxy acetone (DHA) and with other dialkyl viologen catalysts. A brown solution forms when the reaction is complete. Fig. 2 shows a control reaction of MV in 1.0 M KOH minus glyceraldehyde. A dark blue solution of reduced MV also forms and eventually turns brown, but the uptake of O_2 is ~10 times slower than with carbohydrate present. The results show that in the presence of glyceraldehyde in 1.0 M KOH, two reactions occur: 1) rapid oxidation of glyceraldehyde by MV and 2) a slower self-reduction of MV in 1–3 M KOH (Fig. 2). This latter reaction was previously attributed [18] to reduction of MV by the KOH solution but a more recent study suggested [19] that one methyl group was released from MV to form methanol, which then reduced the remaining MV forming formaldehyde from methanol. Although dialkyl viologens catalyze carbohydrate oxidation by O_2, this hydrolysis reaction ultimately destroys the dialkyl viologen catalyst and makes the use of dialkyl viologens as catalysts in strong base unacceptable. This complicating hydrolysis reaction is discussed in Section 5.

The difference in O_2-uptake between the reaction of glyceraldehyde (Fig. 1) and the control reaction (Fig. 2) is due to MV-catalyzed O_2-oxidation of glyceraldehyde. The products were shown by ^{13}C NMR to be carbonate, formate and small amounts of
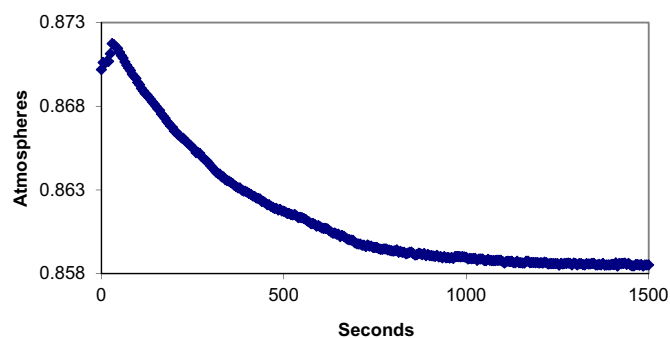

Fig. 1. O_2-uptake during the reaction of MV with glyceraldehlyde in 1.0 M KOH. MV (12.5 μmoles) and glyceraldehyde (12.5 μmoles) were added to 1.0 mL of 1.0 M KOH in a sealed vial and the pressure recorded (O_2-uptake) as a function of time.