

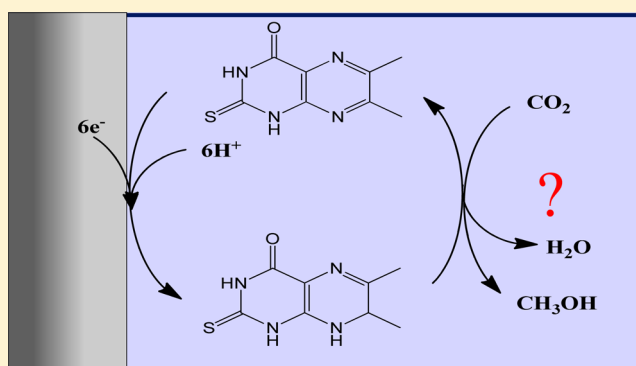
Attempts To Catalyze the Electrochemical CO₂-to-Methanol Conversion by Biomimetic 2e⁻ + 2H⁺ Transferring Molecules

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S Supporting Information

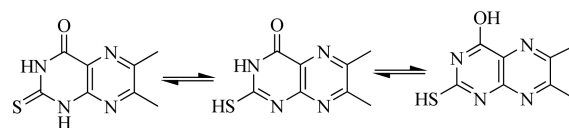
ABSTRACT: In the context of the electrochemical and photochemical conversion of CO₂ to liquid fuels, one of the most important issues of contemporary energy and environmental issues, the possibility of pushing the reduction beyond the CO and formate level and catalytically generate products such as methanol is particularly attractive. Biomimetic 2e⁻ + 2H⁺ is often viewed as a potential hydride donor. This has been the object of a recent interesting attempt (*J. Am. Chem. Soc.* **2014**, *136*, 14007) in which 6,7-dimethyl-4-hydroxy-2-mercaptopteridine was reported as a catalyst of the electrochemical conversion of CO₂ to methanol and formate, based on cyclic voltammetric, ¹³C NMR, IR, and GC analyses. After checking electrolysis at the reported potential and at a more negative potential to speed up the reaction, it appears, on ¹H NMR and gas chromatographic grounds, that there is neither catalysis nor methanol and nor formate production. ¹H NMR (with H₂O presaturation) brings about an unambiguous answer to the eventual production of methanol and formate, much more so than ¹³C NMR, which can even be misleading when no internal standard is used as in the above-mentioned paper. IR analysis is even less conclusive. Use of a GC technique with sufficient sensitivity confirmed the lack of methanol formation. The direct or indirect hydride transfer electrochemical reduction of CO₂ to formate and to methanol remains an open question. Original ideas and efforts such as those discussed here are certainly worth tempting. However, in view of the importance of the stakes, it appears necessary to carefully check reports in this area.



INTRODUCTION

Electrochemical and photochemical conversion of carbon dioxide to liquid fuels is one of the most important issues of contemporary energy and environmental challenges.^{1–4} Although carbon monoxide and formate could be interesting molecules in this respect, further reduced products, such as methanol, are particularly appealing. This is the reason why the report that a molecule as simple as protonated pyridine (pyH⁺) is able to catalyze the conversion of carbon dioxide to methanol at a platinum electrode aroused considerable interest and excitement.⁵ The mechanism of this reaction has been first thought as a set of homogeneous reactions following the reduction of the pyridinium ions (PyH⁺) to the corresponding radical, PyH• that would react with CO₂ to ultimately produce methanol. It has been shown since then that not only this mechanism is not correct but that no methanol is found among the reduction products. PyH⁺ and also CO₃H₂ resulting from the aqution of CO₂ are classically reduced to dihydrogen as other Brønsted acids.⁶ In this context, the report that, based on the hydride transfer properties of the reduced forms of molecules of this family,⁷ 6,7-dimethyl-4-hydroxy-2-mercaptopteridine (PTE, Chart 1) catalyzes the reduction of CO₂ to methanol⁸ aroused great interest.⁹

Chart 1. Tautomeric Forms of PTE



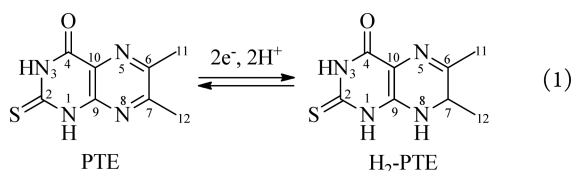
An additional attractive feature of the system is that it involves an electrode material as inert as glassy carbon, which is entailed with a much higher hydrogen overpotential than platinum.

Unfortunately we ran into very serious difficulties when we willingly attempted to test the proposed system. The first of these concerns is the cyclic voltammetric behavior of PTE, which, at variance with ref 8, does not show any variation upon addition of CO₂. It is however conceivable that catalysis might be undetected within the time-scale of cyclic voltammetry and could nevertheless take place during long duration preparative-scale electrolyses.

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This is what is stated in ref 8, even if the formation of 0.1 mM of methanol in the presence of 5 mM “catalyst” after 1 h electrolysis can hardly be named “catalysis”. One could nevertheless argue that some species formed upon electron + proton uptake by PTE could transfer hydride to CO₂, en route to formate and next to methanol even if the process is desperately slow. The main point we wish to make in the present contribution is that these reactions do not occur at all. What happens is simply the 2e⁻ + 2H⁺ reduction of PTE into to 6,7-dimethyl-4-one-2-thione-7,8-dihydropteridine (H₂-PTE) according to reaction 1.



A notable question concerns the potential at which the electrolysis is carried out and its possible influence on products. For this reason, we carried out the electrolysis at two different potentials, first at -0.66 V vs SHE, which allows the complete transformation of PTE into H₂-PTE within a reasonable amount of time, viz. 2 h. We also repeated the same experiment at the same potential as in ref 8,¹⁰ namely -0.46 V vs SHE, at the very foot of the PTE/H₂-PTE wave, which makes, as expected, the complete conversion of PTE into H₂-PTE extremely lengthy viz. 12 h.

We will show in the following:

- (i) The cyclic voltammetric responses of PTE, taken at meaningful values of the scan rate, under argon and as well as under CO₂ simply correspond to the two-electron/two-proton reduction of PTE to H₂-PTE, with no indication of any catalysis of CO₂ reduction.
- (ii) ¹H NMR with H₂O presaturation is the best way of testing the formation of methanol and formate, and its application leads to the conclusion that none of these products are formed either at -0.66 V vs SHE or at -0.46 V vs SHE electrolysis potential.
- (iii) The reported detection of methanol by ¹³C NMR is based on an incorrect interpretation of the spectra caused by the absence of an internal standard. This was shown upon gathering the ¹³C NMR spectra after electrolysis at each of the two above-mentioned potentials.
- (iv) Application of appropriately sensitive GC detection also shows that neither methanol nor formate is produced in the two above-mentioned electrolysis regimes.

RESULTS AND DISCUSSION

Cyclic Voltammetry. The cyclic voltammetric responses in the absence of CO₂ obtained by the authors of ref 8 and by us are significantly different, as shown in Figure 1. The comparison between our results and those of ref 8 involve experiments carried out at a scan rate, $\nu = 0.1$ V/s rather than on other data where the scan rate was as low as 0.001 V/s. Such a low scan rate in the experiment under Ar was used as an introduction to the next experiment under CO₂, because catalysis was expected to be very weak, a very low scan rate was selected hoping to boost the appearance of catalysis. Indeed, as known for a very long time,¹¹ the parameter that controls the magnitude of the catalysis current is not the catalysis rate content, k_{cat} itself, but the dimensionless ratio $\lambda = RTk_{\text{cat}}/F\nu$.

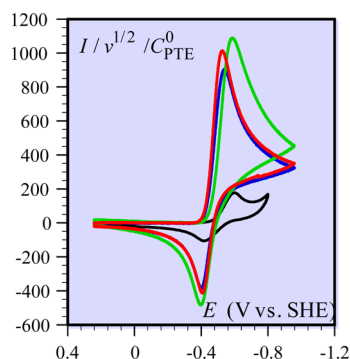


Figure 1. Normalized cyclic voltammetry of 1 mM PTE at a glassy carbon electrode in 0.1 M phosphate buffer + 0.1 M KCl, under argon at pH = 6.3 (green), under CO₂ at pH = 5.9 (red), and under argon at pH = 5.9 (blue). Black: from the blue CV curve in Figure S5 (bottom right) of ref 8 recorded at 0.1 V/s with $C_{\text{PTE}}^0 = 20$ mM. I is the current density in $\mu\text{A}/\text{cm}^2$, ν is the scan rate in V/s, and C_{PTE}^0 is the PTE bulk concentration in mM.

With a very poor k_{cat} , one may thus be tempted to increase λ by decreasing the scan rate, hoping to reach a value that enables catalysis to be evidenced and eventually to derive a value of k_{cat} . However, the temptation of using such low scan rates for this purpose should be resisted for the following reasons.

All meaningful analyses of cyclic voltammetric data require that it should be borne in mind that it is a transient technique in which linear diffusion is the sole mode of transport of the electroactive species to the exclusion of migration, convection, and spherical-type diffusion.^{11b} At scan rates as low as 0.001 V/s, strong interference of natural convection and spherical-type diffusion is expected, misleadingly affecting the shape and characteristics of the current–potential responses. This is part of the basic rules that should be followed in the practice of cyclic voltammetry as a guaranty that the equations used to treat the experimental data (which are based on the assumption that linear diffusion is the sole mode of transport) do apply. Distortions ensuing from the interference of natural convection when these rules are not respected have been the object of systematic investigations.¹² Neglect of these basic rules may give the impression that a slow catalytic reaction occurs, whereas, in fact, the operator is watching the competition between several modes of transport. A typical example of how such artifacts affect diagnosis and rate constant determination can be found in the corrected analysis⁶ of CV responses in the alleged⁵ catalysis of CO₂-to-methanol electrochemical reduction on platinum.

As seen in Figure 1, the potential location and degree of reversibility of the wave are about the same in the two studies.^{13a} The normalized peak currents however exhibit a significant difference (by a factor of ca. 7), therefore calling for a check of the origin of the PTE samples that have been used in the two studies.^{13b}

The cyclic voltammogram we obtained, as e.g., in Figure 1, fall in line with the well-established quinone-hydroquinone type quasi-reversible two-electron:two-proton reduction¹⁴ (eq 1) of many bio or biomimic molecules including pterins and pteridines.¹⁵

Replacing argon by 1 atm CO₂ produces no significant change in the cyclic voltammogram when the pH of the solution has been adjusted to be the same under argon and under CO₂.

The fact that no catalysis of CO₂ reduction occurs within the time-scale of meaningful scan rates in cyclic voltammetry does not exclude that it may take place over longer time periods. This was investigated by preparative-scale electrolysis experiment as described below.

Electrolyses. Electrolyses were performed under argon or carbon dioxide, in 10 mL of a 0.1 M phosphate buffer/0.1 M KCl solution at pH 6.3 with 5 mM of PTE. At -0.66 V vs SHE it takes about 1 h to observe the charge reaching a plateau at 9.6 Coulombs, corresponding to the complete two-electron reduction of the 5 mM PTE solution into H₂-PTE (Figure 2a). At -0.46 V vs SHE (i.e., -0.65 V vs Ag/AgCl as reported

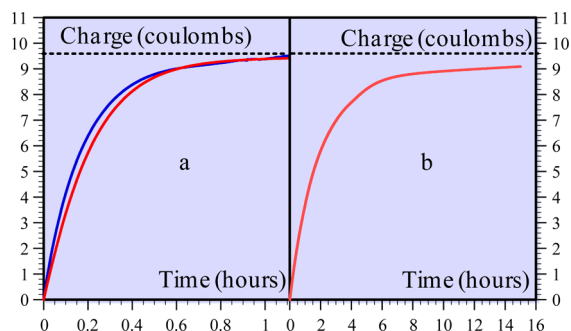


Figure 2. Electrolyses at -0.66 V vs SHE of 5 mM solutions of PTE in 0.1 M phosphate buffer + 0.1 M KCl, under 1 atm argon (blue line) and 1 atm CO₂ (red line). At (a) -0.66 and (b) -0.46 V vs SHE. The dashed horizontal line represents the theoretical value for the complete two-electron reduction of the PTE solution.

in ref 8), ¹H and ¹³C NMR spectra show a mixture of PTE and H₂-PTE, and it takes more than 15 h to completely reduce the 5 mM PTE solution; the charge then reaching a plateau (Figure 2b). No noticeable differences were observed between the argon and the CO₂ purged solutions, as seen in Figure 2a. In other words no catalytic phenomenon could be evidenced from the charge passed during electrolysis under 1 atm CO₂.

We nevertheless took the precaution to check whether any methanol and/or formate could be formed in small amounts as the result of a very slow catalysis, which effect on the charge passed would be too small to be detected.

¹H NMR. ¹H NMR spectroscopy is perfectly suited to methanol detection in water. There is no need to use ¹³CO₂, and the spectra can be run within a minute with a submicromolar detection limit. It is surprising this technique has not been used by the authors of ref 8. All NMR experiments were carried out with *N,N'*-dimethylformamide (DMF) as an internal standard. Under argon, ¹H NMR spectroscopy of PTE with water signal suppression using presaturation shows two singlets at 2.63 and 2.59 ppm (protons on methyl groups C-11 and C-12, respectively) (Figure 3b), which disappear upon reduction at a potential of -0.66 V vs SHE to give one singlet at 2.05 ppm (protons on C-11) and one doublet at 1.26 ppm ($J = 6.6$ Hz, protons on C-12) (Figure 3c). This doublet is due to the coupling between protons on C-12 and the proton on C-7, whose quadruplet cannot be well-resolved as it just stands on the edge of the water signal. This observation indicates that the two-electron/two-proton process consists in the reductive hydrogenation of the N-8–C-7 double bond thus producing the expected H₂-PTE. No noticeable difference could be observed when the same electrolysis experiment was run under 1 atm CO₂ (Figure 3d). The same is true with an electrolysis

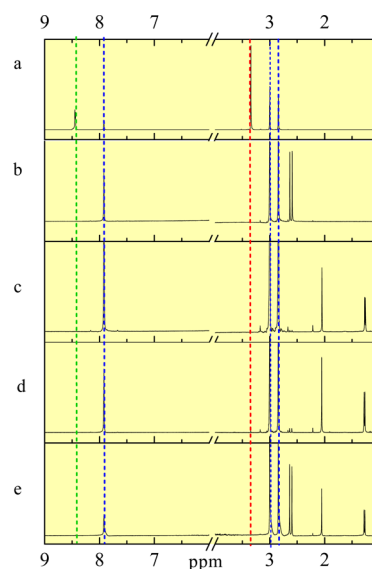


Figure 3. ¹H NMR with presaturation of the water signal of solutions containing 0.1 M of phosphate buffer (pH 6.3), 0.1 M of KCl, and 10 mM DMF. (a) After addition of 20 mM of methanol. (b–e) In the presence of 5 mM PTE: (b) before electrolysis; (c) after 2 h electrolysis under argon at -0.66 V vs SHE; (d) after 2 h electrolysis under 1 atm CO₂ at -0.66 V vs SHE; (e) after 1 h electrolysis under 1 atm CO₂ at -0.46 V vs SHE (same potential as in ref 8). Methanol signal in red, DMF in blue, and formate in green.

potential equal to -0.46 V vs SHE (same potential as in ref 8). Figure 3a shows the spectrum of methanol in the same experimental conditions with the methyl group signal at 3.34 ppm.

The limit of detection for this methanol signal is very low, as we can still observe a well-defined peak at 1 μM methanol (Figure 4), i.e., 5000 times lower than the quantity of PTE. This signal has not been observed in any of the experiments run under CO₂. The same conclusion applies formate as results from the examination of the left-hand part of Figure 3.

¹³C NMR. Cyclic voltammetry, charge passed in electrolysis, and most particularly the very sensitive ¹H NMR analysis of the solutions electrolyzed under CO₂ do no show any indication of

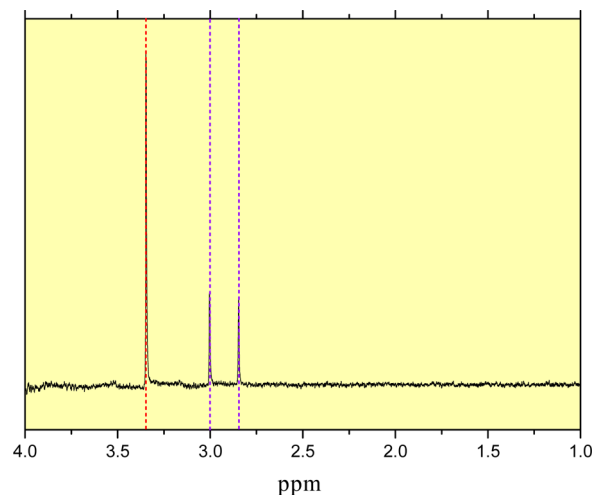


Figure 4. ¹H NMR with presaturation of the water signal of a solution of 1 μM of methanol + DMF in 0.1 M of phosphate buffer (pH 6.3) and 0.1 M of KCl. Methanol signal in red, and DMF in blue.

catalysis producing methanol and formate in the same conditions as those of the ref 8. How come that, in these conditions, analysis by ^{13}C NMR reported in ref 8 indicates that methanol is present in the solutions electrolyzed under CO_2 ?

To resolve this problem and probe the effect of the reduction upon the carbon atoms of the molecule, we performed a series of JMOD and DEPT-90 NMR experiments¹⁶ on the pre- and post-electrolyzed solutions, under an argon and under a CO_2 atmosphere. The interest of this cross-examination is that JMOD shows CH and CH_3 signals antiphase with respect to CH_2 and C_{quat} carbons, while DEPT-90 only shows CH signals. It is thus possible to track the reductive transformation of PTE and to see whether or not methanol is formed. Indeed, a signal would be seen using JMOD, and this signal should disappear when DEPT-90 is run. After electrolysis at either -0.66 or -0.46 (as in ref 8) V vs SHE, the spectrum is the same whether the experiment is run under argon or under CO_2 (Figure 5, JMOD). The two methyl group C-11 and C-12 signals are shifted to 22.69 and 19.13 ppm. A new signal appears at 50.58 ppm. It is close but not the same as the peak of methanol (49.70 ppm). This is where the confusion in ref 8 arose, worsened by the lack of internal reference. Comparison between the JMOD and DEPT-90 NMR experiments finishes to lift any ambiguity: If this signal were that of methanol, it should have disappeared when passing from JMOD and DEPT-90 as seen in JMOD and DEPT-90 Figures 5a. The fact that it remains proves that it does not correspond to methanol but rather to the C-7 of H_2 -PTE.

We may thus conclude that ^{13}C NMR analysis of the electrolyzed solutions is also perfectly compatible with the lack of catalysis and methanol formation.

GC. We come now to gas chromatography analysis of the solutions electrolyzed in the same conditions as described earlier. As in ref 8, the electrolyzed solution of PTE was passed through an Amberlite IRN-150 ion exchange column to extract ionic species (potassium chloride and sodium phosphate salts). Standard solutions of known methanol concentrations were analyzed, and the retention time for the peak of methanol was determined at 2.1 min (Figure 6a). Using a chromatograph equipped with a FID detector (full description of instrumentation and procedures in the SI), the limit of detection for aqueous solutions of methanol was determined to be below $1\ \mu\text{M}$. Due to the sensitivity of the apparatus, special cleaning care was done to prevent the apparition of the methanol peak even after cleaning the syringe thoroughly with water. It is thus important to start the acquisition of the chromatograms with the postelectrolysis solution and do the methanol calibration curve afterward, with increasing amount of methanol to prevent major errors. The chromatogram showed no trace of methanol (Figure 6a), and the small peaks observed are well below the $1\ \mu\text{M}$ methanol peak signal (as compared to the 5 mM of the initial PTE). From these experiments, we can again conclude that no methanol was produced during the electrolysis under a CO_2 atmosphere. The way in which methanol was analyzed by GC in ref 8 is summarized in Figure 6b showing that the sensitivity in the concentration range of interest was quite uncertain (curiously the calibration curve did not go through the origin).

CONCLUSION

Cyclic voltammetry, preparative-scale electrolysis, and analysis of the electrolyzed solution by means of ^1H NMR, ^{13}C NMR, and GC analysis of electrolyzed solutions all converge to

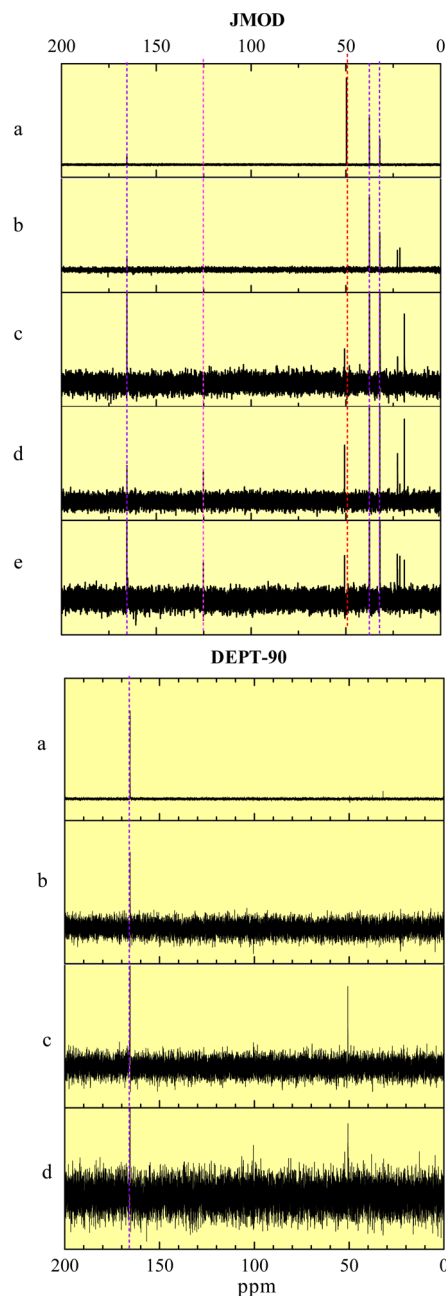


Figure 5. JMOD and DEP 90 ^{13}C NMR of solutions containing 0.1 M of phosphate buffer (pH 6.3), 0.1 M of KCl, and 10 mM DMF. (a) After addition of 20 mM of methanol. (b–e) In the presence of 5 mM PTE: (b) before electrolysis; (c) after 2 h electrolysis under argon at -0.66 V vs SHE; (d) after 2 h electrolysis under 1 atm CO_2 at -0.66 V vs SHE; and (e) after 1 h electrolysis under 1 atm CO_2 at -0.46 V vs SHE (same potential as in ref 8). Methanol signal in red, DMF in blue, CO_2 in magenta.

unambiguously show the $2\text{e}^- + 2\text{H}^+$ 6,7-dimethyl-4-hydroxy-2-mercaptopteridine/6,7-dimethyl-4-one-2-thione-7,8-dihydrop-teridine couple does not catalyze the reduction of CO_2 into methanol or formate. The direct or indirect hydride transfer electrochemical reduction of CO_2 to formate and to methanol remains an open question. Original ideas and efforts such as those developed in ref 8 are certainly worth tempting. However, in view of the importance of the stakes, it appears necessary to carefully check reports in this area to avoid illusory future orientations.

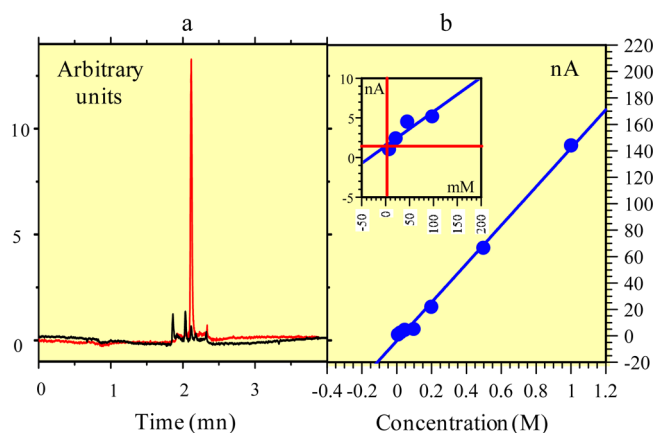


Figure 6. (a) In black: gas chromatography (see text and SI) of a 0.1 M of phosphate buffer (pH 6.3) + 0.1 M of KCl after electrolysis under 1 atm CO₂ at -0.64 V vs SHE; and in red: in the presence of 1 μ M methanol. (b) Calibration curve of methanol (from Figure S3 in ref 8). The red lines in the inset show how the methanol concentration was determined.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12138.

Materials and methods; and full ¹H NMR spectrum of PTE in acetone-*d*₆ and D₂O (PDF)

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Notes

The authors declare no competing financial interest.

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- (9) It is worth noting however that the methanol concentration reported to be formed after 2 h electrolysis, 100 μ M, is very small as compared to the “catalyst” concentration 5 mM, implying an extremely low turnover frequency catalysis, if any.

(10) In spite of the fact that the effect of shifting the electrolysis potential toward more negative values, if any, should be to increase the formation of hydride transfer products (formate and methanol) at the expense of H₂, due to ensuing increased depletion of the proton concentration at the electrode surface.

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(13) (a) The larger anodic-to-cathodic peak potential separation in ref 8 is presumably due to the lack of ohmic drop compensation. (b) There is no indication of the origin of the PTE used in ref 8. In our case, 6,7-dimethyl-4-hydroxy-2-mercapto-pteridine (or the tautomer form 6,7-dimethyl-4-one-2-thionepteridine) was obtained from Sigma-Aldrich. Its ¹H NMR spectrum in acetone agrees with literature data (see Supporting Information).

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