

Table I. Second-Order Rate Constants for Carbon Dioxide Insertion into *cis*-CH₃W(CO)₄L⁻ Derivatives^a

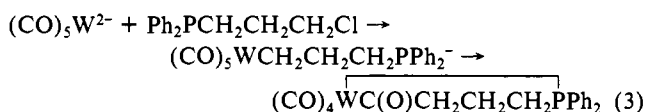
L	k ₂ , s ⁻¹ M ⁻¹	relative rates
CO	3.46 × 10 ⁻⁶	1
P(OMe) ₃	2.00 × 10 ⁻⁴	57.8
PMe ₃	8.40 × 10 ⁻⁴	243

^a Reactions carried out in tetrahydrofuran at 25 °C at a carbon dioxide pressure of 760 torr. The products, *cis*-CH₃CO₂W(CO)₄L⁻, have been prepared by more conventional approaches elsewhere and characterized spectroscopically as well as X-ray crystallographically.¹⁵

contains an ORTEP drawing of the anion, *cis*-CH₃W(CO)₄PMe₃⁻, along with pertinent bond distances. Unfortunately we have not thus far been able to obtain X-ray quality crystals of the parent salt containing the CH₃W(CO)₅⁻ anion for comparative purposes. However, the structure of the isoelectronic neutral species, CH₃Re(CO)₅, has been determined by electron diffraction.¹² The Re-C(CH₃) bond distance was found to be 2.308 (17) Å, or somewhat longer than that found in *cis*-CH₃W(CO)₄PMe₃⁻, where the W-C(CH₃) distance is 2.18 (3) Å. On the basis of the expected effect on the M-C(CH₃) bond upon going from CH₃-Re(CO)₅ to CH₃W(CO)₅⁻, the W-C(CH₃) bond in the latter species is anticipated to be somewhat longer than that observed in the analogous neutral rhenium species and the herein reported tungsten PMe₃ substituted derivative. This similarity in metal-ligand bond distances is seen in the (CO)₅ReCl¹³ and (CO)₅WCl⁻¹⁴ species, where the M-Cl bond distances are 2.515 (2) and 2.566 (2) Å, respectively.

Substitution at the metal center by phosphorus donor ligands is found to greatly expedite the CO₂ insertion process, where the second-order rate constant (Table I) increases in value by 2 orders of magnitude upon replacing CO by PMe₃ or P(OMe)₃.^{15,16} As expected the more basic PMe₃ ligand has a greater effect. Temperature-dependent studies were carried out at atmospheric CO₂ pressure employing the *cis*-CH₃W(CO)₄P(OMe)₃⁻ substrate, resulting in activation parameters of ΔH^{*} = 10.2 kcal mol⁻¹ and ΔS^{*} = -43.3 eu. These parameters are quite consistent with the proposed concerted mechanism for carbon dioxide insertion.

A similar rate enhancement was noted for CO₂ insertion into the W-C bond in the chelating (CO)₄WCH₂CH₂CH₂PPh₂⁻ derivative. This latter species was prepared by thermal decarboxylation of the stable (CO)₄WC(O)CH₂CH₂CH₂PPh₂⁻ species¹⁷ which resulted from reaction 3.^{18,19}



(11) Single crystals of [PNP][*cis*-CH₃W(CO)₄PMe₃] were grown from THF/toluene/hexane (1:1:1) at 0 °C. They belong to the monoclinic space group C₂ with a = 16.538 (8) Å, b = 17.102 (9) Å, c = 16.106 (7) Å, β = 115.26 (3)°, V = 4119.7 Å³. R(weighted) = 4.35% for 4034 reflections with I > 3σ(I). Crystallographic analysis was carried out by the crystallographic staff of Molecular Structure Corp.: Dr. M. W. Extine, R. A. Peascoe, Dr. J. M. Troup, and B. B. Warrington (details to be published separately).

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(16) The concentration of CO₂ in tetrahydrofuran at 25 °C and 760 torr is ca. 0.332 M. This datum and other CO₂ solubility data as a function of temperature were taken from: Endre, B.; Bor, G.; Marta, M. S.; Gabor, M.; Bela, M.; Geza, S. *Veszpremi Vegyip. Egy. Kozl.* **1957**, *1*, 89.

(17) The chelating acyl derivative has been characterized by X-ray crystallography. Crystals of this salt suitable for X-ray analysis were grown from THF/toluene at 10 °C. They belong to the monoclinic space group P2₁/c with a = 9.444 (1) Å, b = 22.654 (5) Å, c = 21.279 (4) Å, β = 96.00 (1) Å³, R(weighted) = 6.1% for 1693 reflections with I > 3σ(I). Crystallographic analysis was carried out by Dr. Terry Delord at TAMU. Details to be published separately.

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Since crystallographic data do not indicate a weakening of the W-C(CH₃) bond upon substitution by sterically nonencumbering phosphine ligands, the propensity for CO₂ insertion into M-C bonds involving electron-rich metal centers can be assumed to arise from an enhanced interaction of the CO₂ molecule with these centers. Studies are continuing to further assess the details of these carbon dioxide insertion processes.

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 83-08281) is greatly appreciated.

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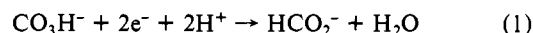
Electrochemical Reduction of Aqueous Bicarbonate to Formate with High Current Efficiency Near the Thermodynamic Potential at Chemically Derivatized Electrodes

Charles J. Stalder, Shuchi Chao, and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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We wish to report results that show that the electrochemical reduction of aqueous CO₃H⁻ to HCO₂⁻, eq 1, can be effected with



high current efficiency and near the thermodynamic potential using chemically derivatized metallic electrodes represented by Figure 1. We note that CO₃H⁻(aq) is a CO₂ equivalent: H₂O + CO₂ ⇌ H₂CO₃ ⇌ CO₃H⁻ + H⁺ ⇌ CO₃²⁻ + 2H⁺. The reduction of aqueous CO₂ is known to occur at many electrode surfaces,¹⁻⁴ but generally the reduction requires a significantly more negative electrode potential than thermodynamically demanded. Our work was stimulated by the discovery^{5,6} that supported Pd is an effective catalyst for the reaction of CO₃H⁻ with H₂ to form HCO₂⁻. The Pd-impregnated polymer, [(PQ²⁺)_n]_{surf}, on semiconductor or metallic electrodes illustrated in Figure 1 has been shown to be an effective catalyst for H₂ evolution.⁷ We have subsequently shown⁶ that the Pd-impregnated [(PQ²⁺)_n] system is capable of catalyzing the reaction of H₂ with CO₃H⁻ to form HCO₂⁻. In the electrochemical experiments described below, the [(PQ²⁺)_n] redox polymer provides a mechanism to bring the reducing equivalents to the high surface area Pd catalyst sites. The E^o's of the [(PQ^{2+/+/0})_n]_{surf} system are -0.55 and -0.90 V vs. SCE,⁷⁻⁹ negative enough to bring the Pd particles to a sufficiently reducing

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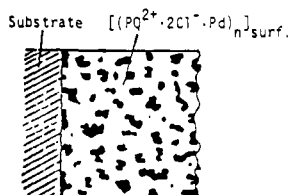
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Table I. Electrochemical Reduction of Aqueous CO_3H^- at Catalytic Electrodes^a

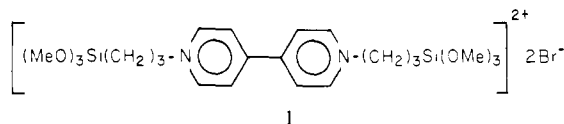
cathode (area, cm^2)	PQ^{2+} coverage, mol/cm^2	catholyte ^b	total charge passed, C	$[\text{HCO}_2^-]$, M^c	current efficiency, %
W/ $[(\text{PQ}^{2+}\cdot\text{Pd})_n]$ (29.7)	3.9×10^{-8}	1.0 M Na $[\text{CO}_3\text{H}]$	45	0.016	56
W/ $[(\text{PQ}^{2+}\cdot\text{Pd})_n]$ (22.2)	6.8×10^{-8}	1.0 M Na $[\text{CO}_3\text{H}]$	205	0.046	36
W/ $[(\text{PQ}^{2+}\cdot\text{Pd})_n]$ (16.0)	9.0×10^{-8}	1.0 M Na $[\text{CO}_3\text{H}]$	174	0.064	57
W/ $[(\text{PQ}^{2+}\cdot\text{Pd})_n]$ (17.1)	1.2×10^{-7}	1.0 M Na $[\text{CO}_3\text{H}]$	163	0.09 ₀	80
W/ $[(\text{PQ}^{2+}\cdot\text{Pd})_n]$ (15.1)	1.3×10^{-7}	3.0 M Cs $[\text{CO}_3\text{H}]$	286	0.15	81
Pt/ $[(\text{PQ}^{2+}\cdot\text{Pd})_n]$ (19.5)	1.3×10^{-7}	1.0 M Na $[\text{CO}_3\text{H}]$	181	0.08 ₀	40
Pt/ $[(\text{PQ}^{2+}\cdot\text{Pd})_n]$ (19.5)	1.4×10^{-7}	1.0 M Na $[\text{CO}_3\text{H}]$	107	0.09 ₀	78
Pt/ $[(\text{PQ}^{2+}\cdot\text{Pd})_n]$ (19.5)	1.1×10^{-7}	7 M Cs $[\text{CO}_3\text{H}]$	439	0.26	85
W/ $[(\text{PQ}^{2+}\cdot\text{Pt})_n]$ (19.1)	1.0×10^{-7}	1.0 M Na $[\text{CO}_3\text{H}]$	164	trace	<1

^aAll experiments were carried out as described in the text; in no case was the electrode potential moved more negative than -0.8 V vs. SCE. The initial current densities were in the vicinity of $100 \mu\text{A}/\text{cm}^2$ at ~ -0.7 V vs. SCE and eventually decline to $<50 \mu\text{A}/\text{cm}^2$ even upon moving the potential to -0.8 , V vs. SCE. ^bThis concentration is approximate since CO_2 is easily evolved from solution in the initial deoxygenation. The actual CO_2 content of the solutions is lower since 1.0 M Na $[\text{CO}_3\text{H}]$ and 7.0 M Cs $[\text{CO}_3\text{H}]$ represent the approximate solubility limits and there is ~ 1 atm CO_2 above such solutions. ^cMonitored by ^1H or ^{13}C NMR or by enzyme assay, ref 11. The error limit is $\pm 10\%$.

**Figure 1.** Catalytic electrode for reduction of aqueous CO_3H^- .

potential to reduce CO_3H^- ; $E^\circ(\text{CO}_3\text{H}^-/\text{HCO}_2^-) \approx -0.76$ V vs. SCE.¹⁰ We now detail experiments showing that the electrochemical reduction represented by eq 1 can yield significant amounts of HCO_2^- using large surface area, chemically derivatized electrodes near the thermodynamic potential.

The chemically derivatized electrodes represented by Figure 1 were prepared as previously described⁷⁻⁹ with reagent I as the



monomer from which the surface-confined polymer, $[(\text{PQ}^{2+})_n]$, can be grown. For the experiments described here, the electrode material was a coil of W wire or Pt gauze exposing $15\text{--}30 \text{ cm}^2$ of geometrical area that were derivatized by cycling the potential at 50 mV/s between -0.3 and -0.75 V vs. SCE in an aqueous 0.1 M phosphate solution containing $1\text{--}3 \text{ mM}$ of I. The amount of $[(\text{PQ}^{2+})_n]$ confined to the surface was monitored by integrating the charge associated with the $[(\text{PQ}^{2+})_n] \rightleftharpoons [(\text{PQ}^+)_n]$ interconversion in a 1.0 M KCl electrolyte. The derivatization was continued to achieve a coverage of 4×10^{-8} to $1.4 \times 10^{-7} \text{ mol}/\text{cm}^2$ of PQ^{2+} units. This corresponds to a dry thickness of polymer of $0.1\text{--}1 \mu\text{m}$.^{8,9} Impregnation of the $[(\text{PQ}^{2+})_n]$ with Pd was effected by dipping the W/ $[(\text{PQ}^{2+}\cdot 2\text{Cl}^-)_n]$ electrode into an aqueous solution of 3 mM K_2PdCl_4 for 15 min to exchange the 2Cl^- for PdCl_4^{2-} to yield M/ $[(\text{PQ}^{2+}\cdot\text{PdCl}_4^{2-})_n]$.⁷ The reduction of PdCl_4^{2-} to Pd was effected by placing the M/ $[(\text{PQ}^{2+}\cdot\text{PdCl}_4^{2-})_n]$ in a 0.1 M KCl solution and immediately cycling the potential from -0.3 to -0.75 V vs. SCE where the $[(\text{PQ}^{2+})_n]$ is completely reduced to $[(\text{PQ}^+)_n]$, which is capable of reducing PdCl_4^{2-} to Pd.⁷ The derivatized electrode was withdrawn from the KCl solution after completely oxidizing the polymer system by potentiostating at -0.3 V vs. SCE for several seconds to yield $[(\text{PQ}^{2+}\cdot 2\text{Cl}^-\cdot\text{Pd})_n]$. Often this Pd-impregnation procedure was repeated once to increase the amount of Pd in the polymer. Such electrodes were then used immediately in aqueous CO_3H^- solutions to effect electrochemical formation of HCO_2^- .

(10) The value of $E^\circ(\text{CO}_3\text{H}^-/\text{HCO}_2^-)$ is estimated from the knowledge^{5,6} that the equilibrium constant for the reaction $\text{H}_2 + \text{CO}_3\text{H}^- \rightleftharpoons \text{HCO}_2^- + \text{H}_2\text{O}$ is about unity. This means that $E^\circ(\text{CO}_3\text{H}^-/\text{HCO}_2^-) \approx E^\circ(\text{H}_2\text{O}/\text{H}_2)$ at pH 8.9) = -0.76 V vs. SCE.

Table I summarizes the results from a number of electrolyses. Typically, the M/ $[(\text{PQ}^{2+}\cdot 2\text{Cl}^-\cdot\text{Pd})_n]$ cathodes were placed in one compartment of a two-compartment electrochemical cell using a known, but minimum, volume ($<10 \text{ mL}$) of an aqueous CO_3H^- solution. A saturated calomel reference electrode (SCE) was placed in the catholyte, and a Pt counterelectrode was placed in the anode compartment containing the same aqueous electrolyte as in the cathode compartment. The cell was covered with Parafilm to minimize exposure to O_2 and loss of H_2 . The potential of the cathode was controlled with a potentiostat and the charge was measured using a coulometer. The potential of the cathode was slowly moved from an initial value of -0.2 V vs. SCE to a more negative value to bring and maintain a significant cathodic current of $\sim 1\text{--}3 \text{ mA}$. Usually, this involved bringing the potential to ~ -0.7 V vs. SCE. Instantaneous movement to -0.7 V vs. SCE results in a large current that gives H_2 gas evolution sufficient to destroy the integrity of the electrode/polymer interface. As the electrolyses continued, the potential was moved more negative (but never beyond ~ -0.80 V) to maintain a significant cathodic current. Aliquots of catholyte were removed periodically and analyzed for HCO_2^- by ^1H and/or ^{13}C NMR or by using an enzyme assay.¹¹

The results allow several conclusions. First, the electrolysis of the ^{13}C -enriched CO_3H^- unambiguously establishes that reduction of the added CO_3H^- to HCO_2^- occurs. Additionally, the ^{13}C NMR does not reveal any other reduced carbon-containing products. The presence of a single resonance at an intensity $>5\%$ of that for $\text{H}^{13}\text{CO}_2^-$ should have been observable. Second, a comparison of charge passed and HCO_2^- produced shows a high current efficiency. The overall efficiency can exceed 80% , though the current efficiency is sometimes significantly lower. Presumably, low initial current efficiency is attributable in part to the formation of Pd hydride, $\text{Pd} + x\text{H}^+ + xe^- \rightarrow \text{PdH}_x$, the reduction of the polymer itself, $[(\text{PQ}^{2+})_n] + ne^- \rightarrow [(\text{PQ}^+)_n]$, and direct H_2 generation. Ultimately, a less than 100% current efficiency is consistent with the fact that the Pd is a catalyst for the $\text{CO}_3\text{H}^- + \text{H}_2 \rightleftharpoons \text{HCO}_2^- + \text{H}_2\text{O}$ equilibrium where the equilibrium constant is about one.⁶ Additionally, in long-term experiments HCO_2^- is found in the anode compartment via diffusion through the fine glass frit separator. Third, the reduction of CO_3H^- occurs within 80 mV of the standard potential. As the electrolyses proceed the more negative potentials required to sustain current flow are a consequence of the buildup of reduction product. We are not presently able to identify the active form of the CO_2 equivalent reduced at Pd; CO_3^{2-} , CO_3H^- , and CO_2 are all present at their equilibrium amounts under the conditions used. The significance here rests in the reduction of the aqueous CO_2 near the thermodynamic potential with a reasonable rate and high current efficiency.

There is some degradation in the performance of the catalytic electrode with time, but the amount of HCO_2^- produced far

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exceeds the amount of catalytic material (Pd or polymer) by a significant factor (over 1000 molecules of HCO_2^- per Pd atom added have been obtained). Also, the rate of reduction of CO_3H^- is slow, but the highest concentration of HCO_2^- produced is significant, up to 0.25 M. Producing higher concentrations of HCO_2^- should be possible, particularly if a better charge carrier than the $[(\text{PQ}^{2+/+})_n]$ can be found. The most negative potentials used allow reduction of the polymer partially to the $[(\text{PQ}^0)_n]$ state that is much less durable in aqueous electrolyte than is the $[(\text{PQ}^+)_n]$ state.^{8,9} Additionally, the rate could be improved, since Pd on C has been shown⁶ to be more active than the Pd-impregnated $[(\text{PQ}^{2+/+})_n]$ when using H_2 as the reductant. Even as the results stand, the current density of $\sim 100 \mu\text{A}/\text{cm}^2$ for reduction of CO_3H^- to HCO_2^- near the thermodynamic potential shows that C-H bond formation from a CO_2 equivalent can occur electrochemically under mild conditions. As in the catalyzed reaction of H_2 with CO_3H^- , we find that under the same conditions where Pd-impregnated $[(\text{PQ}^{2+/+})_n]$ is an effective catalyst, the analogous Pt system has negligible activity. Spectroscopic studies of catalytic electrodes before and after use are under way to establish possible reasons for the differences between the Pt and Pd.

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Registry No. 1, 74173-49-2; PdCl_4^{2-} , 14349-67-8; W, 7440-33-7; Pt, 7440-06-4; Pd, 7440-05-3; CO_3H^- , 71-52-3; HCO_2^- , 71-47-6.

Ribooligonucleotides, r(C-G-C-G) Analogues Containing 8-Substituted Guanosine Residues, Form Left-Handed Duplexes with Z-Form-like Structure

Seiichi Uesugi, Mitsuru Ohkubo, Hidehito Urata, Morio Ikehara,* Yuji Kobayashi, and Yoshimasa Kyogoku

Faculty of Pharmaceutical Sciences
and Institute for Protein Research
Osaka University, Suita, Osaka 565, Japan
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The discovery of a left-handed DNA duplex structure (Z DNA) in d(C-G-C-G-C-G) crystals¹ has generated a great deal of interest in oligo- and polydeoxyribonucleotides containing alternating pyrimidine-purine sequences. In Z DNA, the dG residues adopt an unusual syn conformation about the glycosidic bond with C3'-endo furanose ring puckering while the dC residues take an anti and C2'-endo forms similar to those in B DNA. Oligo[d(C-G)]'s adopt the Z-form structure in solution at high salt concentrations.^{2,3} However, corresponding ribooligonucleotides, oligo[r(C-G)]'s, do not take the Z-form structure under similar conditions.⁴ Recently, we have suggested the possible existence of Z-form structure in RNA duplexes by conformational study of a r(C-G) analogue⁵ containing 8-bromoguanosine (br^8G), which

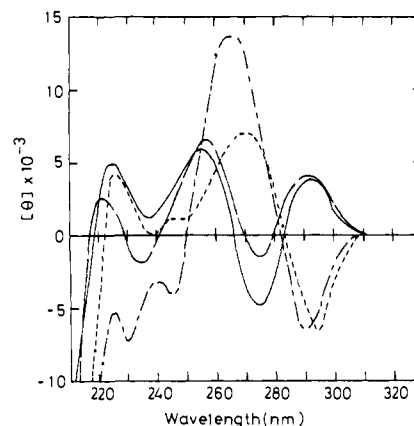


Figure 1. CD spectra of r(C-br⁸G-C-br⁸G) (—), r(C-m⁸G-C-m⁸G) (---), r(C-G-C-G) (· · ·), and d(C-G-C-G-C-G) (· · · · ·) at 0 °C. The ribotetramers (1 A_{260} unit/mL) were measured in 0.1 M NaCl, 0.01 M phosphate buffer (pH 7.5). The deoxyhexamer (1 A_{260} unit/mL) was measured in 4 M NaCl, 0.01 M phosphate buffer (pH 7.5).

tends to adopt the syn conformation.^{6,7} For characterization of Z RNA duplexes, however, the chain length ought to be at least four because the repeating unit in the Z-form structure is a dinucleotide.

In this communication, we report the synthesis and characterization of r(C-br⁸G-C-br⁸G) and r(C-m⁸G-C-m⁸G). 8-Methylguanosine (m⁸G) also has a tendency to adopt the syn conformation.⁸ Studies on the tetramers by UV, CD, and ^1H NMR spectroscopy reveal that they form duplexes similar to that of Z DNA as observed for oligo[d(C-G)]'s in high salt solutions.³

r(C-br⁸G-C-br⁸G) and r(C-m⁸G-C-m⁸G) were synthesized by a phosphotriester method.^{9,10} r(C-br⁸G-C-br⁸G) was synthesized by a dimer block condensation, and r(C-m⁸G-C-m⁸G) was synthesized by a stepwise condensation method. The tetramers obtained could be completely hydrolyzed by nuclease P1 to give C, pbr⁸G (or pm⁸G), and pC in 1:2:1 ratio.

The CD spectra of the modified tetramers at 1 °C are shown in Figure 1. The spectra of d(C-G-C-G-C-G) in 4 M NaCl and of r(C-G-C-G) in 0.1 M NaCl are also included. All the oligomers here were shown to form duplexes under the conditions in Figure 1 by UV and CD spectroscopy.¹¹ The r(C-G-C-G) analogues give spectra very similar in pattern and magnitude (λ_{max} 's at around 225, 255, and 290 nm and λ_{min} 's at around 235 and 275 nm).¹² Their CD patterns in the 260–310-nm region are quite different from that of d(C-G-C-G-C-G) in 4 M NaCl where the Z DNA structure is adopted. However, the CD spectrum of r(C-G-C-G), which has been proved to take an A-form structure,⁴ is similar to that of d(C-G-C-G-C-G) in 4 M NaCl in this region. The clear inversion of signs of the 290-nm bands observed between r(C-G-C-G) and its 8-substituted derivatives strongly suggests that the modified tetramers may form left-handed duplexes.

In order to elucidate the conformations of the modified tetramer duplexes, ^1H NMR spectra were measured at various temperatures. Resonances of the base protons and some of the sugar protons were assigned by extensive ^1H - ^1H decoupling and nuclear Overhauser effect (NOE) experiments. r(C-br⁸G-C-br⁸G) and r(C-m⁸G-C-m⁸G) showed similar chemical shift-temperature profiles for each proton suggesting that both tetramers have similar duplex structures.¹³ NOE experiments on the m⁸G-containing

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(12) CD spectral patterns of the modified tetramers in 4 M NaCl were similar to those in 0.1 M NaCl. T_m 's of the modified tetramer duplexes increased with increasing salt concentration (at least up to 4 M NaCl).

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