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O-Atom Exchange between H_2O and CO_2 Mediated by a Bis(dithiolene)tungsten Complex

Junhyeok Seo and Eunsuk Kim*

Department of Chemistry, Brown University, Providence, Rhode Island 02912, United States

Ⓢ *Supporting Information*

ABSTRACT: Inspired by the CO_2-reductatse activity of tungsten-dependent formate dehydrogenases (W-FDHs), a reduced W-FDH model, $[W^{IV}(OH)(S_2C_2Ph_2)_2]^-$, was prepared in situ through hydrolysis of $[W^{IV}(OPh)(S_2C_2Ph_2)_2]^-$ (**1**) and its reactivity with CO_2 was investigated. The reaction between $[W^{IV}(OH)(S_2C_2Ph_2)_2]^-$ and CO_2 at room temperature leads to the formation of $[W^{IV}(O)(S_2C_2Ph_2)_2]^{2-}$ (**2**), which slowly oxidizes to $[W^{V}(O)(S_2C_2Ph_2)_2]^-$ (**3**). Isotopic labeling experiments reveal that the O atom in CO_2 incorporates into **3**. This implies that there is carbonic anhydrase like activity, in which carbonation and decarboxylation are mediated by a bis(dithiolene)tungsten complex.

Carbon dioxide (CO_2) has been implicated as one of the main causes for global warming,[1] thus, the transformation of CO_2 into environmentally friendly and valuable chemicals is of great interest. Among the various chemical transformations, the reduction of CO_2 is particularly significant because the reduced forms of CO_2 such as formic acid, methanol, or methane can be directly used as fuels, which establishes CO_2 as an abundant and inexpensive source for alternative energy.[2,3] Conversion of CO_2 to formic acid can be achieved (electro)-chemically. The development of efficient catalysts for such a transformation comprises an active area of research.[2−5] There have been continuing efforts in developing coordination complexes that can catalyze the reduction of CO_2 with H_2,[4] insertion of CO_2 into an M−H bond,[2,5] or electrochemical reduction of CO_2.[3] Although these complexes show much promise, none has shown the comparable efficiency and selectivity of the CO_2-reducing enzymes found in nature.

Formate dehydrogenase (FDHs) are enzymes that catalyze the two-electron oxidation of formate (HCO_2^-) to CO_2 coupled with the reduction of $NAD(P)^+$ to NAD(P)H.[6] In some prokaryotes, the FDHs contain molybdenum (Mo) or tungsten (W) cofactors, by which an efficient CO_2-reductase activity (reduction of CO_2 to formate) has been also observed.[7] Recently, Hirst and co-workers have shown that a purified W-FDH can activate an electrode to reduce CO_2 to formate more efficiently than any of the known synthetic catalysts.[8]

The X-ray structures of several Mo- or W-containing FDHs are known.[9] In the oxidized state, the active site contains a Mo^{VI} or W^{VI} ion in a trigonal-prism geometry with two pyranopterin molecules, one selenocysteine (SeCys), and a sixth −SH (or OH) ligand.[9a−c] The coordination geometry of the reduced FDHs was first determined from *Escherichia coli* Mo-FDH_H, in which Mo^{IV} was in a square-pyramidal geometry with two equatorial pyranopterins and a SeCys axial ligand.[9a] However, the same crystallographic data have been reevaluated more recently,[9d] revealing that the SeCys in the reduced state is no longer coordinated to the metal center. Instead, the −SH (or −OH) has been proposed for the axial ligand[9d] (Figure 1).

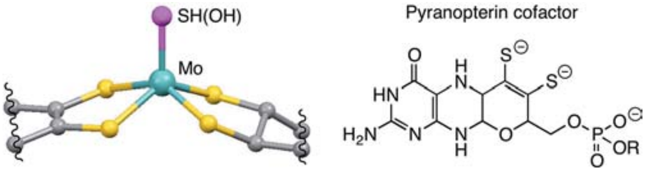

Figure 1. Active-site structures in the reduced Mo-FDH (*E. coli*).[9d]

In light of the reexamined FDH structure[9d] and the efficient electrocatalytic activity of W-FDH,[8] here we report our studies on the CO_2 reactivity of a synthetic model complex of W-FDH.

Synthetic models for FDHs are limited,[10] although a significant number of bis(dithiolene)molybdenum and -tungsten complexes are known.[11] Our own attempts to directly synthesize discrete HO- or HS-bound bis(dithiolene)tungsten analogues have not been successful. However, Holm and co-workers have previously reported[12] that a group of phenolate-bound tungsten or molybdenum bis(dithiolene) complexes undergo hydrolysis in the presence of excess H_2O to yield $W^{IV}{=}O$ complexes via the formation of $\{W^{IV}OH\}$ species. These reports inspired us to explore the CO_2 reactivity of $[W^{IV}(OH)(S_2C_2Ph_2)_2]^-$, which can be prepared in situ through hydrolysis of $[W^{IV}(OPh)(S_2C_2Ph_2)_2]^-$ (**1**) in the presence of H_2O.

We first sought a hydrolysis condition that can be achieved with the minimum amount of H_2O possible in order to favor the binding of CO_2 over H_2O to $[W^{IV}(OH)(S_2C_2Ph_2)_2]^-$. We found that a relatively small amount (10 equiv) of H_2O was sufficient enough to induce hydrolysis of **1**[12b] in acetonitrile to yield $[W^{IV}(O)(S_2C_2Ph_2)_2]^{2-}$ (**2**). However, we noticed that **2** was not stable over 12 h in our reaction conditions, and it slowly converted into another well-known[13] compound, $[W^{V}(O)(S_2C_2Ph_2)_2]^-$ (**3**; Scheme 1), which is likely associated with the reduction of H^+ to hydrogen (vide infra).

IR spectroscopy provides us with rich information that supports the generation of **3** as the final hydrolysis product as well as the released free phenol (Figure 2). The IR spectrum of

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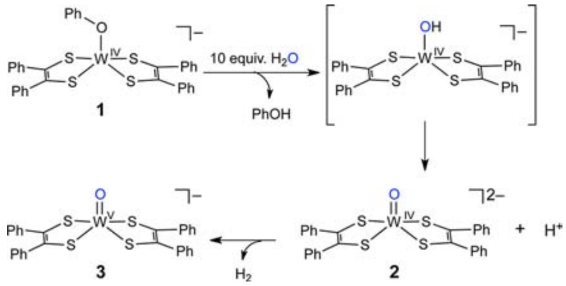
Scheme 1



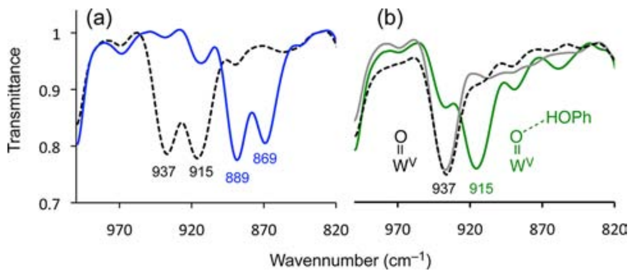


Figure 2. IR spectra (Nujol) of (a) the crude reaction products of **1** and 10 equiv of H_2O (black dotted line) and those of **1** and 10 equiv of $H_2{}^{18}O$ (blue solid line), (b) the isolated reaction product **3** (black dotted line), **3** in the presence of 2 equiv of externally added phenol (green solid line), and reisolated **3** after removal of phenol by precipitation (gray solid line).

the crude reaction products of **1**/H_2O exhibits two strong $W^V{=}O$ frequencies at 937 and 915 cm^{-1}, both of which shift to 889 and 869 cm^{-1} when the reaction is carried out using $H_2{}^{18}O$ (Figure 2a). No such isotopic shifts were observed when independently synthesized **2** or **3** was treated with 10 equiv of $H_2{}^{18}O$.[14] This indicates that the O atoms in the reaction products originate from H_2O through hydrolysis of **1**, during which the intermediate $[W^{IV}(OH)(S_2C_2Ph_2)_2]^-$ must have been generated. The 937 cm^{-1} peak from the crude reaction products is assigned to the stretching frequency of $W^V{=}O$ in **3**, consistent with the literature value.[13] The presence of the additional peak at 915 cm^{-1} is presumably due to the $W^V{=}O$ moiety hydrogen-bonded to free phenol that is released from **1**. Mass spectrometry further confirms the presence of free phenol in the reaction mixture. When **3** was isolated by precipitation with diethyl ether, only the 937 cm^{-1} band was observed in the IR spectrum as expected. However, when the isolated **3** is redissolved in acetonitrile, followed by the addition of phenol, the 915 cm^{-1} peak reappears (Figure 2b).[15] The appearance of the 915 cm^{-1} band is not observed when phenolate (PhO^-) is added to a solution of **3**, which supports the assignment of the 915 cm^{-1} peak for the hydrogen-bonded $W^V{=}O$ moiety. This cycle can be repeated multiple times without causing decomposition of **3**.

To gain insight into the unexpected oxidation of **2** to **3** during hydrolysis, we studied the reactivity of independently synthesized **2** with a proton source. When 1 equiv of HBF_4 was added to an acetonitrile solution of **2** at room temperature, the absorption bands at 350, 449, and 527 nm from **2** decayed with a concomitant formation of **3** (λ_{max} = 720 nm) in the UV−vis spectrum.[16] In addition, the H_2 evolution from the reaction was qualitatively detected from the headspace gas of the reaction flask with a commercial H_2 dosimeter.[16]

Because the formation of $[W^{IV}(OH)(S_2C_2Ph_2)_2]^-$ was implied as an intermediate during our hydrolysis reaction, we studied the desired CO_2 reactivity of **1** in the presence of H_2O. An acetonitrile solution of **1** containing 10 equiv of H_2O was exposed to 1 atmospheric pressure of CO_2 at room temperature for 12 h.[16] To our surprise, **3** was again identified as the final reaction product from the **1**/H_2O/CO_2 reaction, with no indication of generating either the reduced CO_2 products (e.g., formate, CO, oxalate, etc.) or a hydrated product ($HCO_3{}^-$).[17] However, when we carry out the same reaction using 10 equiv of $H_2{}^{18}O$, we observe that only ∼32% of **3** contains the $W{=}{}^{18}O$ moiety (889 and 869 cm^{-1}; Figure 3), suggesting that H_2O is no longer the major source of oxygen in **3**. Because CO_2 is the only other possible O-atom donor in the reaction mixture, the reaction was further evaluated by using $C^{18}O_2$. When the reaction was carried out using ^{18}O-enriched CO_2 (85% $C^{18}O_2$) and H_2O, ∼50% of $W{=}{}^{18}O$ complexes were observed in the reaction products, confirming that the O atom in CO_2 incorporates into **3**.[16]

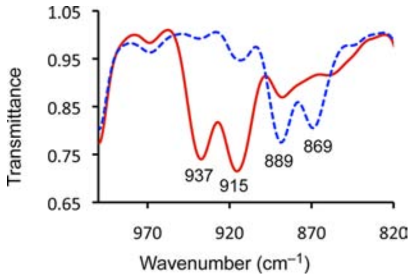
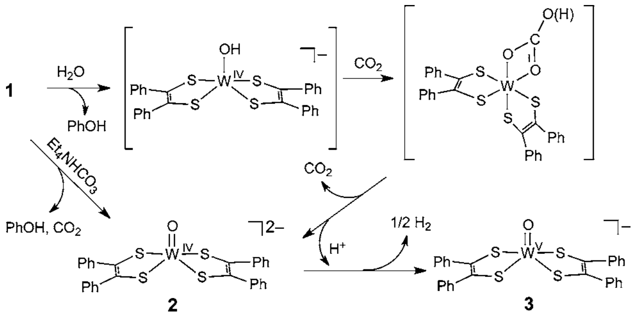


Figure 3. IR spectra (Nujol) of the crude reaction products of **1**/$H_2{}^{18}O$ (10 equiv)/CO_2 (red solid line) and those of **1**/$H_2{}^{18}O$ (10 equiv) (blue dotted line).

Complex **1** does not react with CO_2 in dry solvent under the same experimental conditions, suggesting that the formation of the $\{W^{IV}OH\}$ moiety is crucial to initiating reactivity with CO_2. This behavior along with the absence of any carbon-containing reaction products derived from CO_2 lead us to conclude that the reaction of **1**/CO_2/H_2O does not exhibit the anticipated FDH activity. Instead, $[W^{IV}(OH)(S_2C_2Ph_2)_2]^-$ reacts with CO_2 to form a presumable bicarbonato or carbonato intermediate, which immediately undergoes decarboxylation to generate $[W^{IV}(O)(S_2C_2Ph_2)_2]^-$ (**2**) and CO_2 (Scheme 2). The formation of (bi)carbonato species from CO_2 with a metal hydroxide is common for many transition-metal complexes,[18] and examples of tungsten(IV) carbonato complexes exist.[19] In our reaction, however, the (bi)carbonato species does not appear to be stable probably because of the oxophilic character

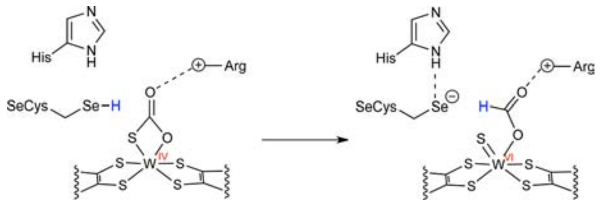
Scheme 2



of tungsten(IV) in a bis(dithiolene) ligand environment. In fact, with the only exception of FDHs, all other known bis(pyranopterin)-bound tungsten/molybdenum enzymes catalyze the O-atom-abstraction chemistry.[6] In order to evaluate the prospect of the proposed (bi)carbonato intermediate during the reaction (Scheme 2), **1** was reacted with 1 equiv of Et_4NHCO_3. Upon the addition of bicarbonate to **1**, the oxo compound **2** formed immediately, as monitored by UV−vis spectroscopy.[16] The result supports a notion that the O atom of CO_2 is inserted into **2** through a (bi)carbonate-bound tungsten intermediate.

The FDHs utilize a bis(dithiolene)-bound M^{IV} (M = Mo or W) ion to reduce CO_2 to formate. The use of higher-valent metal ions with noninnocent ligands by the enzyme is a strategy very different from that of most synthetic systems in which the metal ions in much lower valences, 0, 1+, and 2+, are utilized to activate CO_2.[20] Our current study shows that the presence of a nucleophilic ligand such as OH^- is crucial to initiating CO_2 reactivity with a bis(dithiolene)tungsten(IV) species to likely form a tungsten (bi)carbonate intermediate. Indeed, a recent calculation study[21] on the mechanism of Mo-FDH suggests that a Mo(IV) thiocarbonato intermediate forms during the oxidation cycle of formate to CO_2. With respect to the reverse reaction by W-FDH, one can expect the conversion of W(IV) thiocarbonate species to W(VI) formate (Scheme 3), similar to the typical O-atom-abstraction chemistry known for this class of enzyme.[6] In our current synthetic model system, however, we were not able to imitate the reduction step. This may be due to the lack of a proton delivery channel near the metal active site, i.e., selenocysteine and histidine, that is strictly conserved in the FDH proteins.

Scheme 3



In summary, we have studied the CO_2 reactivity of a structural analogue of W-FDH. A bis(dithiolene)tungsten complex **1** itself does not react with CO_2 at ambient temperature. However, an in situ generated hydrolysis product, $[W^{IV}(OH)(S_2C_2Ph_2)_2]^-$, reacts with CO_2 and displays a carbonic anhydrase like activity. A tungsten (bi)carbonate species is presumed to form during the reaction. Future studies will focus on the factors critical to inducing an O-atom abstraction from a putative tungsten (bi)carbonate intermediate over the oxide (O^{2-}) abstraction chemistry observed in this study.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and UV−vis and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Eunsuk_Kim@brown.edu.

Notes

The authors declare no competing financial interest.

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(14) Syntheses of **2** and **3** are known.[13]

(15) The complete conversion of the 937 to 915 cm^{-1} peak requires at least 3 equiv of phenol.[16] Upon substitution of phenol with *p*-nitrophenol, the 915 cm^{-1} peak further shifts to 910 cm^{-1}.[16]

(16) See the Supporting Information.

(17) The ^{13}C NMR and IR spectra of the reaction mixtures of **1**/H_2O/$^{13}CO_2$ did not display any signals for the CO_2-redrived products. The chemical detections for CO using Fe^{II}(TPP) and $Cp^*RuCl(PCy_3)$ were also negative.

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