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**Water Splitting**

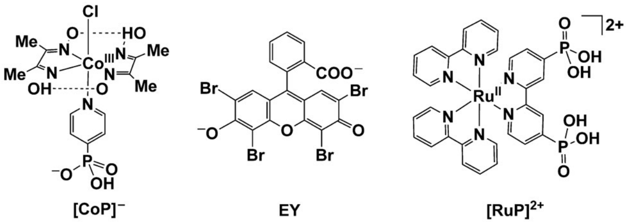
# Selective Reduction of Aqueous Protons to Hydrogen with a Synthetic Cobaloxime Catalyst in the Presence of Atmospheric Oxygen**

*Fezile Lakadamyali, Masaru Kato, Nicoleta M. Muresan, and Erwin Reisner**

Sunlight provides us with a practically endless amount of carbon-neutral energy and there is currently great interest in harvesting some of this electromagnetic energy for the production of a solar fuel.[1] An attractive approach is sunlight-driven water splitting, where renewable $H_2$ and the by-product $O_2$ are released simultaneously from water during irradiation.[2] An economical $H_2$-evolution catalyst must not only contain inexpensive materials, but must also be active under $O_2$ during turnover, because a real-world device will be exposed to atmospheric $O_2$ and produce $O_2$ in situ as a result of water splitting.

Noble-metal catalysts such as platinum are excellent $H_2$-evolution catalysts, but they are expensive and show cross-selectivity for the reduction of $O_2$.[3] In biology, the [FeFe]- and [NiFe]-hydrogenases are $H_2$-evolution catalysts that work at high rates and small over-potentials.[4] However, isolated hydrogenases are fragile and often extremely sensitive towards $O_2$.[5] Many significant advances were reported recently in the development of small-molecule $H_2$-evolution catalysts.[6] Nevertheless, there has been very little progress in the development of homogeneous $H_2$-generating catalysts that operate in the presence of $O_2$. A noteworthy exception is an expensive rhodium catalyst that operates under $O_2$.[7] To the best of our knowledge, there are no reports of small-molecule 3d transition-metal catalysts that reduce protons efficiently under high levels of $O_2$.

Herein, we report on an inexpensive cobalt catalyst that evolves $H_2$ electro- and photocatalytically in pH-neutral water and in the presence of atmospheric $O_2$. We employ $(Et_3NH)[Co^{III}Cl(dimethylglyoximato)_2(pyridyl\text{-}4\text{-}hydrophosphonate)]$ ($(Et_3NH)[CoP]$, Scheme 1), which is a member of cobaloxime-type catalysts that currently receive much attention in electrochemical and photochemical applications.[8] The phosphonic acid group in $(Et_3NH)[CoP]$ enables the complex to dissolve in water and allows for its immobilization on metal oxide surfaces for heterogeneous applications.[8f,9]



*Scheme 1.* Chemical structures of the cobalt catalyst $[CoP]^-$, the organic dye eosin Y (EY), and the ruthenium dye $[RuP]^{2+}$.

First, we studied the electrocatalytic activity of the complex anion $[CoP]^-$ in a pH-neutral electrolyte solution in the absence and presence of air (21% $O_2$ in $N_2$). Cyclic voltammetry (CV) scans were recorded in a three-electrode cell with $(Et_3NH)[CoP]$ (1 mM) on a glassy carbon working electrode in an aqueous solution of triethanolamine (TEOA) and $Na_2SO_4$ (0.1 M each) at pH 7 and 25 °C. A cathodic wave at $E_p = -0.13$ V versus the normal hydrogen electrode (NHE), assigned to the $Co^{III} \rightarrow Co^{II}$ reduction process, and reduction of $Co^{II}$ with the onset of electrocatalytic proton reduction at approximately $-0.55$ V versus NHE was observed at a scan rate of 100 $mV\,s^{-1}$ under a $N_2$ atmosphere (Figure 1 a, dashed

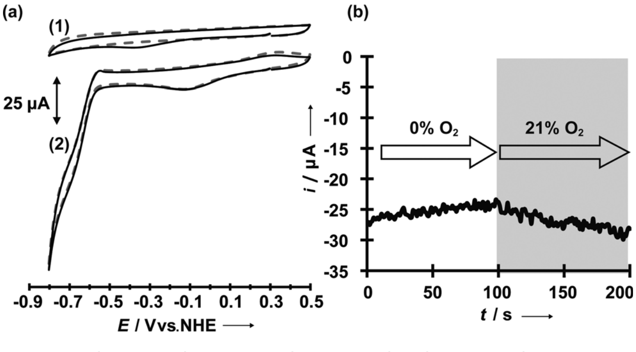


*Figure 1.* Electrocatalytic $H_2$ production in the absence and presence of atmospheric $O_2$. a) CV scans at a scan rate of 0.1 $V\,s^{-1}$ (1) without catalyst (control experiment) and (2) in the presence of $(Et_3NH)[CoP]$ (1 mM). Dashed traces were recorded under a $N_2$ atmosphere and the solid traces under 21% $O_2$ in $N_2$. b) Chronoamperometry of $(Et_3NH)[CoP]$ (1 mM) at $-0.7$ V versus NHE. The measurement was started under $N_2$ and the electrochemical cell was flushed with air after 100 s (gray shading). In all experiments, a glassy carbon working (3 mm diameter), a Pt counter, and a Ag/AgCl reference electrode were employed and the measurements were carried out in an aqueous solution of TEOA/$Na_2SO_4$ (0.1 M each, pH 7) at 25 °C.

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trace). This voltammetric response is consistent with previous reports of cobaloximes under an inert atmosphere.[2g,10]

CV scans of $(Et_3NH)[CoP]$ exposed to air showed a very similar voltammetric response. No additional waves were observed from the reduction of $O_2$, and the same potential–current curves were maintained for proton reduction (Figure 1a, solid trace). Thus, 21 % $O_2$ has only a marginal effect on the electrocatalytic activity of $[CoP]^-$ on the short time scale of a CV experiment. Figure 1b shows the results of chronoamperometric measurements of a stirred solution of $(Et_3NH)[CoP]$ (1 mM) in a pH 7 solution of $TEOA/Na_2SO_4$ (0.1M) at −0.7 V versus NHE. A constant catalytic current (−27 to −25 μA) was observed under $N_2$. After 100 s, the headspace of the cell was flushed with air, which resulted in only a minor increase in the current from −25 to −30 μA. This experiment confirms that air has only a small effect on the catalytic activity of $[CoP]^-$.

Controlled-potential electrolysis allowed us to explore the tolerance of $[CoP]^-$ towards $O_2$ over a longer time scale and to determine the Faradaic yield of electrocatalytic $H_2$ evolution. We used a closed electrochemical cell with $(Et_3NH)[CoP]$ (0.5 mM) in a stirred aqueous solution of $TEOA/Na_2SO_4$ at pH 7 and applied potential of −0.7 V versus NHE on a large-area glassy carbon working electrode (ca. 2 $cm^2$) for two hours. A gas chromatograph was used to quantify the amount of $H_2$ for the determination of the Faradaic efficiency in our system. The passage of an average of 5.5 C of charge under a $N_2$ atmosphere resulted in 22 μmol $H_2$ in the headspace, whereas 6.6 C and 17 μmol $H_2$ were observed under atmospheric $O_2$. These values correspond to a respectable Faradaic efficiency of $(68\pm3)$ % under $N_2$ and $(43\pm4)$% under 21 % $O_2$ in $N_2$ (see Table S1 in the Supporting Information). No hydrogen was detectable after electrolysis without $[CoP]^-$. Controlled potential electrolysis, therefore, confirms that the catalyst retains its activity over a prolonged time scale (at least for 2 h), with good selectivity for proton reduction under atmospheric $O_2$. Previously, only the electrocatalytic reduction of $O_2$ and no evolution of $H_2$ was reported in electrochemical studies with cobaloxime-type catalysts in the presence of $O_2$.[11]

Subsequently, we explored the photocatalytic activity of $[CoP]^-$ in homogeneous and heterogeneous systems in the presence of $O_2$. Our electrochemical studies demonstrated that $[CoP]^-$ was active under air, but possible quenching of the excited state of a chromophore and formation of reactive oxygen species could easily prevent a photochemical system operating in the presence of $O_2$. For a homogeneous system, we selected the organic dye eosin Y (EY, used as its disodium salt, $Na_2EY$, Scheme 1). EY had previously been employed as a photosensitizer with cobalt-based proton reduction catalysts such as $[Co^{III}Cl(dimethylglyoximato)_2(pyridine)]$[12] and $[Co^{II}(bipy)_3]Cl_2$[13] (bipy = 2,2′-bipyridine) under an inert atmosphere. The multicomponent system works as follows: photoexcitation of EY results in the formation of a triplet excited state (*EY), which can either inject electrons directly into a cobalt catalyst or be reductively quenched by an electron donor (e.g., TEOA), followed by injection of the electron into a cobalt complex.[12]

A homogeneous solution of $(Et_3NH)[CoP]$ (0.2 μmol) and $Na_2EY$ (0.1 μmol) was exposed to visible light (solar light simulator; 100 $mW\,cm^{-2}$, $\lambda > 420$ nm) in an aqueous solution of TEOA (4.5 mL, 0.1M) at pH 7 and 25 °C. After irradiation of the mixture for one hour under $N_2$ (containing 2 % $CH_4$ as internal GC standard), $(12.5\pm0.6)$ μmol $H_2$ evolved (Figure 2a; headspace volume: 4.85 mL). This result corresponds to a cobalt-based turnover frequency ($TOF_{Co}$) of $(62\pm3)$ mol $H_2$ per mol $[CoP]^-$ per hour and a dye-based turnover frequency ($TOF_{EY}$) of $(125\pm6)$ mol $H_2$ per mol EY per hour. The homogeneous system is photoactive between 1 and 2 h, whereupon a turnover number for $[CoP]^-$ ($TON_{Co}$) of $(73\pm4)$ mol $H_2$ per mol $[CoP]^-$ was obtained. The catalytic activity of $[CoP]^-$ in organic-solvent-free aqueous solution compares favorably to other homogeneous photocatalytic systems, where organic solvents are typically added to water and inert conditions are required. One example is $[Ni(P_2^{Ph}N_2^{Ph})_2](BF_4)_2$ ($P_2^{Ph}N_2^{Ph}$ = 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane), which shows a light-driven $H_2$ production TOF of 20 $h^{-1}$ in a water/acetonitrile mixture under $N_2$.[14]

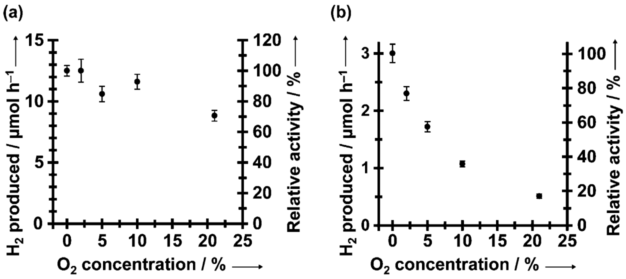

***Figure 2.*** Photocatalytic $H_2$ production in the presence of various concentrations of $O_2$. Visible-light-driven ($\lambda > 420$ nm, 100 $mW\,cm^{-2}$) $H_2$ production rates versus concentration of $O_2$ with a) a homogeneous system consisting of $[CoP]^-$ and EY and b) a heterogeneous system with $[CoP]^-$ and $[RuP]^{2+}$ co-attached to $TiO_2$ nanoparticles (5 mg) at 25 °C. An aqueous solution of TEOA as a sacrificial electron donor was used (4.5 mL. 0.1 M, pH 7), and 0.2 μmol of $(Et_3NH)[CoP]$ and 0.1 μmol of the dye (EY or $[RuP]^{2+}$) were used. Relative $H_2$ production activity (%) to the activity under an inert atmosphere is also shown.

Exposing the homogeneous system to various concentrations of $O_2$ resulted only in a small decrease in the photoinduced $H_2$-evolution activity, and $(70\pm4)$% activity remained in the presence of 21 % $O_2$ compared to that under an inert atmosphere (Figure 2a, see also Table S2 in the Supporting Information). The homogeneous system consisting of $[CoP]^-$ and EY in an aqueous solution of TEOA is, therefore, highly robust in the presence of $O_2$: the catalyst $[CoP]^-$ tolerates high concentrations of $O_2$, and *EY (or a reductively quenched, reduced EY) can inject electrons efficiently into $[CoP]^-$ despite a potential quenching mechanism by $O_2$.[15]

Finally, we studied the photocatalytic activity in a heterogeneous system consisting of $(Et_3NH)[CoP]$ (0.2 μmol) and the tris(bipyridine)ruthenium dye $[RuP]^{2+}$ (0.1 μmol, used as the dibromide salt $[RuP]Br_2$, Scheme 1) co-attached to P25 $TiO_2$ nanoparticles (21 nm diameter, 5 mg).[8f,10d,16] In this heterogeneous system, photoexcitation of $[\mathrm{RuP}]^{2+}$ results in $[{}^{*}\mathrm{RuP}]^{2+}$ and ultrafast electron injection into the conduction band of $TiO_2$, followed by transfer of the $TiO_2$ photoelectrons to $[\mathrm{CoP}]^{-}$ for $H_2$ evolution.[10d] Under $N_2$ with 2% $CH_4$, irradiation ($\lambda > 420$ nm) of $[\mathrm{RuP}]^{2+}/[\mathrm{CoP}]^{-}$-modified $TiO_2$ in TEOA solution (4.5 mL, 0.1M, pH 7) with visible light resulted in $(3.0 \pm 0.2)$ μmol $H_2\,h^{-1}$ and a $\mathrm{TOF}_{\mathbf{Co}}$ of $(15.0 \pm 0.8)$ mol $H_2$ per mol $[\mathrm{CoP}]^{-}$ per hour.[8f,10d,16] The heterogeneous system is photoactive for approximately 10 h with a $\mathrm{TON}_{\mathrm{Co}}$ of $(108 \pm 9)$ mol $H_2$ per mol $[\mathrm{CoP}]^{-}$.

Figure 2 b shows the effect of various amounts of $O_2$ on the photocatalytic activity of $[\mathrm{RuP}]^{2+}/[\mathrm{CoP}]^{-}$-modified $TiO_2$ nanoparticles: increasing the amount of $O_2$ from zero to 21% resulted in a decrease in photoactivity from $(3.0 \pm 0.2)$ to $(0.51 \pm 0.04)$ μmol $H_2\,h^{-1}$ (see Table S3 in the Supporting Information). Therefore, approximately 17% of the $H_2$ production activity remained under 21% $O_2$ in $N_2$ for the colloidal system. There are several possible quenching mechanisms of $[\mathrm{RuP}]^{2+}$-sensitized $TiO_2$ by $O_2$. Electron injection on the picosecond time scale from $[{}^{*}\mathrm{RuP}]^{2+}$ to $TiO_2$ makes energy transfer from $[{}^{*}\mathrm{RuP}]^{2+}$ to $O_2$ unlikely.[10d,17] However, a long-lived $TiO_2$ conduction band electron is formed during irradiation, which can either recombine with oxidized $[\mathrm{RuP}]^{2+}$ or reduce $O_2$ to superoxide radicals ($O_2^{\cdot -}$). These radicals were shown to result in a significant increase in the $[\mathrm{RuP}]^{2+}$ desorption rate from the $TiO_2$ surface,[18] which could decrease the $H_2$ production activity in our heterogeneous system.

In summary, we have described an inexpensive cobalt catalyst $[\mathrm{CoP}]^{-}$ which evolves $H_2$ catalytically under highly desirable conditions: room temperature, pH-neutral water and atmospheric $O_2$. Electrochemical studies show that $[\mathrm{CoP}]^{-}$ has good selectivity for the electrocatalytic reduction of protons under air. We also demonstrated that $[\mathrm{CoP}]^{-}$ can be exploited in photochemical reactions under high levels of $O_2$. The homogeneous system consisting of EY and $[\mathrm{CoP}]^{-}$ remains highly photoactive in the presence of 21% $O_2$, whereas the heterogeneous system with $[\mathrm{CoP}]^{-}$ and $[\mathrm{RuP}]^{2+}$ co-attached to $TiO_2$ nanoparticles also keeps some of the photocatalytic activity for the reduction of aqueous protons. These findings are rationalized by the high selectivity of $[\mathrm{CoP}]^{-}$ for $H_2$ evolution and slow quenching of the excited *EY (or reduced EY) and $TiO_2$ photoelectrons by $O_2$. The low solubility of $O_2$ in water (0.27 mmol $L^{-1}$ at 25 °C under 1 atm of air)[19] might explain in part why our electro- and photocatalytic systems with $[\mathrm{CoP}]^{-}$ operate under atmospheric $O_2$. Work is underway to develop a solar water splitting system, where $H_2$ and $O_2$ evolve simultaneously.

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