Photocatalysis

Microsecond X-ray Absorption Spectroscopy Identification of Co\(^1\) Intermediates in Cobaloxime-Catalyzed Hydrogen Evolution

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Abstract: Rational development of efficient photocatalytic systems for hydrogen production requires understanding of the catalytic mechanism and detailed information about the geometric structure of intermediates in the catalytic cycle. We demonstrate how time-resolved X-ray absorption spectroscopy in the microsecond time range can be used to identify such intermediates and to determine their local geometric structure. This method was used to obtain the solution structure of the Co\(^1\) intermediate of cobaloxime, which is a non-noble metal catalyst for solar hydrogen production from water. Distances between cobalt and the nearest ligands including two solvent molecules and displacement of the cobalt atom out of plane formed by the planar ligands have been determined. Combining in situ X-ray absorption and UV/Vis data, we demonstrate how slight modification of the catalyst structure can lead to the formation of a catalytically inactive Co\(^2\) state under similar conditions. Possible deactivation mechanisms are discussed.

Light-driven catalytic systems for hydrogen evolution from water are crucial components of our energy future.\(^{[1, 2]}\) Efficient photocatalytic hydrogen evolution systems contain platinum nanoparticles or other noble metals that are expensive and of limited availability. This has triggered the development of catalysts based on earth-abundant 3d elements, such as cobalt, iron, and nickel.\(^{[3–9]}\) Cobaloximes are perspective and popular hydrogen-evolving molecular catalysts\(^{[7–9]}\) and they have been implemented in many homogeneous multicomponent photocatalytic systems.\(^{[7, 10–16]}\) The Co\(^{II}\) complex [Co(dmgH)\(_2\)pyCl] (Co\(_1\), dmgH\(_2\) = dimethylglyoxime, py = pyridine Scheme 1) with proton bridges between dmg\(^2–\) ligands and the Co\(^1\) complex [Co(dpgBF\(_3\)_2L\(_2\)] (Co\(_2\), L = H\(_2\)O or CH\(_3\)CN) with (BF\(_3\)) bridges are the two most-studied cobaloxime platforms so far. Rational optimization of such systems, however, depends on our understanding of the catalytic cycle and the possible routes that lead to deactivation.

Different reaction mechanisms for hydrogen evolution have been proposed that involve homolysis\(^{[14, 17, 18]}\) or protonation of a cobalt–hydride bond\(^{[17, 20, 22]}\). They all involve a primary Co\(^{I}\) intermediate which is then protonated to yield a Co\(^{III}\) hydride species. Such a Co\(^{I}\) intermediate has been observed for an analogue of Co\(_2\), [Co(dpgBF\(_3\)_2L\(_2\)] (dpgH\(_2\) = diphenylglyoxime, L = CH\(_3\)CN), by optical flash photolysis in the presence of the photosensitizer [Ru(bpy)\(_3\)]\(^2+\) and methyl viologen (MV\(^{2+}\)) as the electron relay\(^{[21]}\). The latter oxidatively quenches the excited state of the photosensitizer and delivers the electron to the catalyst (Figure 1, top panel). In the absence of a sacrificial electron donor, charge recombination returns the system to its initial state. The solution structure of the Co\(^{I}\) intermediate has been predicted using DFT\(^{[17, 20, 22]}\), but was never experimentally probed. A crystal structure of the Co\(^{I}\) derivative [Co(dpgBF\(_3\)_2(CH\(_3\)CN)]\(^–\) has been reported\(^{[18]}\), but the structure of the intermediate in solution can be significantly different from those in the solid phase. Here, we combine in situ time-resolved X-ray absorption near edge structure (XANES) spectroscopy and UV/Visible spectroscopy to investigate the early stages of hydrogen evolution mediated by Co\(_1\) and Co\(_2\) catalysts. We report the first experimental determination of the structure of the Co\(^{I}\) intermediate formed from Co\(_2\) in solution.
and highlight a major difference in terms of reactivity and stability between Co2 and Co1 under photocatalytic conditions.

XANES spectra contain element-specific information about the structure of metal complexes.\cite{21-23} Time-resolved X-ray absorption spectroscopy in the laser pump- X-ray probe mode was initially established for experiments in the picosecond–nanosecond time range.\cite{26,27} We recently extended the technique to the microsecond range (pump-sequential-probe\cite{29} and pump-flow-probe\cite{28} methods, see the Supporting Information). These new setups coupled with state of the art simulations enables establishing the time-resolved XANES as a powerful tool to study the local structure of catalytic intermediates in light-driven reactions.\cite{29}

The transiently formed Co intermediate (Figure 1, top) was monitored using time-resolved Co K-edge XANES. The sample consisted of Co2, \([\text{Ru(bpy)}_3]^{2+}\), and \(\text{MV}^{2+}\) in acetonitrile. NBuPF6 (0.1 m) was added to control ion pairing and the ionic strength of the solution. A series of 200 Co K-edge XANES spectra corresponding to the time range (−50, 50) μs has been collected using the pump-sequential-probes method.\cite{28} Analysis of these spectra using principal component analysis (PCA)\cite{30,31} indicated that only one intermediate is present in this time series. This intermediate is formed within the first microsecond after the excitation of the photosensitizer. Figure 2 displays the spectrum of Co2 in its initial Co5 state (top panel) and the component corresponding to the transiently formed intermediate (bottom panel, ⋯⋯⋯). To access longer delays we performed the experiment on the same system using the pump-flow-probe method.\cite{29} A similar transient signal was measured at 100 μs delay (Figure 2, ⋯⋯⋯). The positive signal of the transient XANES in the region of the rising edge (7715–7730 eV) is indicative of cobalt reduction. Thus Co1 is the only intermediate that is formed transiently in this multicomponent system over the timeframe 0.5–100 μs. The formation of a CoIII species\cite{21} from the reaction of oxidized photosensitizer \([\text{Ru(bpy)}_3]^{3+}\) and Co2 was not observed.

Accumulation of Co in the presence of a sacrificial electron donor (Figure 1, bottom) has been monitored using in situ UV/Vis spectroscopy. The systems contained CH3CN solutions of Co2, triethanolamine (TEOA), \([\text{Ir(ppy)}_3(bpy)]^+\) (ppy = phenylpyridine), or Eosin Y as the photosensitizer and NBuPF6 (0.1 m). The formation of the CoI state of Co2 is evidenced by the characteristic two-band spectrum with maxima at 556 and 627 nm (Figure 3 and Figure S6 in the Supporting Information). The spectrum is in agreement with the references obtained for electrosynthetically\cite{32} and chemically reduced\cite{19} Co derivatives of Co2 and with ab initio calculations.\cite{32} Results are similar to those reported using a platinum-based photosensitizer\cite{11} and to those observed in the microsecond range at transient conditions for \([\text{Co(dpgBF}_2]_2(\text{CH}_3\text{CN})_2]^{21}\) \(\text{Hydrogen is evolved under accumulation conditions which agrees with the previous report.}\) Thus Co intermediates of Co2 formed either transiently or under photoaccumulation conditions are identical and active for hydrogen evolution.

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Figure 1. Two reaction pathways leading to the formation of CoI intermediates. Top panel: transient formation of a CoI intermediate in the presence of an electron relay (ER) followed by recombination with the oxidized photosensitizer (PS). Bottom panel: accumulation of CoI species in the presence of a sacrificial electron donor (D).

Figure 2. Top panel: Experimental Co K-edge XANES of the initial CoII state of Co2 in acetonitrile. Bottom panel: Transient Co K-edge XANES spectrum corresponding to 100 μs delay after laser excitation (⋯⋯⋯) of a \([\text{Ru(bpy)}_3]^{2+}/\text{MV}^{2+}/\text{Co2}\) system in a pump-flow-probe setup; transient Co K-edge XANES extracted using PCA from the series of 200 spectra measured on the same system in the time range (−50, 50) μs (⋯⋯⋯) with regard to the laser pulse in a pump-sequential-probe setup; the difference between the spectrum of the Co state accumulated for a system containing CoI and Eosin Y in the presence of TEOA as the sacrificial electron donor and the corresponding spectrum of CoI in acetonitrile (⋯⋯⋯). The spectrum obtained using the pump-flow-probe method was multiplied by 2.5 and shifted up, while the spectrum measured at accumulative conditions was divided by 21 and shifted down to simplify visual comparison.
Theoretical modelling of the XANES spectra for Co\textsuperscript{2} and the transiently formed Co\textsuperscript{1} intermediate allows the determination of their structure in solution. Two parameters were varied for Co\textsuperscript{2}: the average distance between cobalt and nitrogen atoms in dmg\textsuperscript{2–} ligands (defined as rigid groups) and the bond length between cobalt and axial nitrogen atoms of the CH\textsubscript{3}CN molecules. For the Co\textsuperscript{1} intermediate state we similarly varied the average distance between the cobalt center and nitrogen atoms of dmg\textsuperscript{2–} ligands and allowed variations in the distances between cobalt and axial ligands independently in opposite directions, that is, not excluding a transition from a six- towards a five-coordinated model. Additionally the displacement of the cobalt atom out of plane formed by nitrogen atoms of dmg\textsuperscript{2–} has been included into the model. The best simulated spectra for the Co\textsuperscript{1} and the Co\textsuperscript{2} species are compared with the experimental data in Figure 4. The model of Co\textsuperscript{1} is characterized by a Co–N(dmg\textsuperscript{2–}) bond length of 1.86 Å, whereas the Co–N(CH\textsubscript{3}CN) distance is 2.02 Å. For the Co\textsuperscript{2} intermediate the best-fitted Co–N(dmg\textsuperscript{2–}) bond length is 1.88 Å, the Co–N(CH\textsubscript{3}CN) lengths are 2.00 and 2.11 Å and the out of plane cobalt displacement is 0.08 Å. Thus, one of the axial bonds remains unchanged from the initial Co\textsuperscript{2} state while the other axial bond becomes slightly weaker. This model is thus at variance with the averaged distance between cobalt and nitrogen atoms of dmg\textsuperscript{2–} ligands (defined as rigid groups) and the bond length between cobalt and axial nitrogen atoms of the CH\textsubscript{3}CN molecules. The structure of such an accumulated state is significantly different from that of the transiently formed Co\textsuperscript{1} intermediate.

UV/Vis monitoring of the same solution confirmed these observations. A transition from the Co\textsuperscript{3} to the Co\textsuperscript{1} state was first observed as a new absorption band at ~430 nm, assigned to a d–d transition for the d\textsuperscript{7} Co\textsuperscript{1} ion (Figures S7 and S8, Supporting Information). However neither typical signatures of the Co\textsuperscript{1} state nor the hydrogen evolution were observed upon longer irradiation. Further investigations indicated that water is required to observe both the typical signal of a Co\textsuperscript{1} intermediate and hydrogen evolution (Figure S9, Supporting Information, and previous reports\cite{12,15}). Thus both Co K-edge XANES and UV/visible measurements indicate that the Co\textsuperscript{1} state accumulated during long-term irradiation in the presence of a sacrificial electron donor with Co\textsuperscript{1} is different from the transiently formed Co\textsuperscript{1} intermediate observed with Co\textsuperscript{2}.

The Co\textsuperscript{1} and Co\textsuperscript{2} systems differ by the bridge between oxime functions in the equatorial plane and by the presence of an axial pyridine ligand in Co\textsuperscript{1}. To discriminate between these two differences, we prepared [Co(dmgBF\textsubscript{3})\textsubscript{2}pyCl\textsubscript{3}] (Co\textsuperscript{3}) (synthesis is described in the Supporting Information) and monitored by UV/visible spectra under similar photocatalytic
conditions. A CoⅠ intermediate with two-band spectrum (identi-
cal to that observed for CoⅡ) was found (Figure S10, Support-
ing Information). Pyridine is a stronger ligand than TEOA that
excludes that a coordination bond between TEOA or its de-
composition product and the cobalt could be responsible for
the difference observed in the CoⅠ states in the above experi-
ments. XANES spectra show such an interaction between sacri-
ficial electron donor and CoⅡ in the CoⅠ state (Figure S5, Sup-
porting Information). However, the amplitude of the spectral
changes at the rising edge of XANES (7715–7730 eV) is much
smaller than the difference observed between the accumulat-
ed and transiently formed CoⅠ species at similar energies. The
difference in behavior between CoⅡ and CoⅠ may thus be as-
tioned to the nature of the bridge in the equatorial planes.
Simulations indicate that the bridge between dmг2− ligands
does not influence the shape of XANES spectra significantly
(Figure S4, Supporting Information) and therefore more severe
modifications have to be found to explain this spectral differ-
ence.

Substituting the proton for (BF2) bridges cathodically shifts the
CoⅤ potential by 500 mV[30] and significantly increases the
nucleophilicity of the CoⅠ center. We thus expected the CoⅠ
intermediate of CoⅠ to rapidly react with any source of protons
in the medium, and specifically with the protons released by
TEOA upon oxidation. Our data, however, show that this
system is unable to evolve hydrogen, probably because of the
limited amount of available protons and the quite basic condi-
tions of the medium. Instead it may degrade through hydride
transfer to the dmгH− ligand.[34,35] Alternatively, the initial CoⅠ
intermediate may react with an iminium species resulting from
the decomposition of TEOA and generate a CoⅢ-alkyl spe-
cies.[36] In both cases, the resulting CoⅢ species can be reduced
to the CoⅠ state through light-driven electron transfers. Howev-
er, due to the significant modification of their electronic struc-
ture, it is unlikely that the corresponding CoⅢ species exhibits
absorption bands in the 550–650 nm region corresponding to
transitions from a metal d orbital to π orbitals delocalized over
imine bonds.[37] Such severe modifications are also in line with
the major difference observed in the Co K-edge XANES spec-
trum (Figure 2) and the lack of hydrogen evolution activity ob-
served for the accumulated CoⅠ state of CoⅠ.

In conclusion, we presented the first structural determina-
tion of intermediates of photocatalytic systems observed in
the microsecond range using time-resolved XANES. The solu-
tion structure of the CoⅠ intermediate of CoⅡ indicates that
only one axial solvent ligand of the cobalt center is labilized,
but not fully displaced as it is observed in the solid state.
While such a CoⅠ intermediate is the resting state of the CoⅡ-
based photocatalytic system, we showed that another catalyt-
cally inactive CoⅠ species forms under similar conditions when
CoⅠ is used as the catalytic platform. Further work can be fo-
cused on the other intermediates (in particular CoⅢH) of coba-
loxime catalysts. The time-resolved XANES method that has
been illustrated in this work can be generally applied to clarify
the photocatalytic mechanism not only for hydrogen-evolving
systems but also for other molecular photocatalysts.

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