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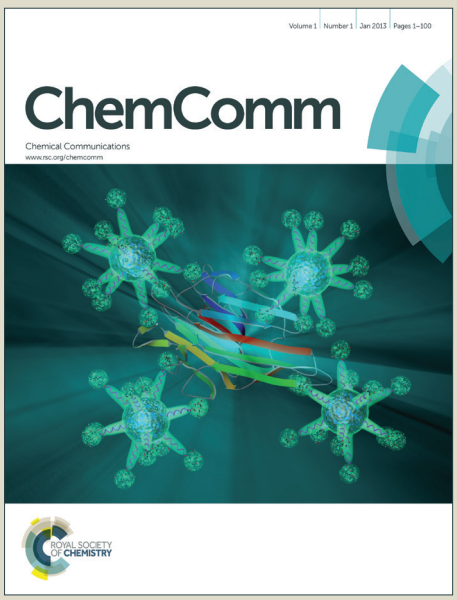

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Ascorbate as Electron Relay Between an Irreversible Electron Donor and a Ru(II) or Re(I) Photosensitizer

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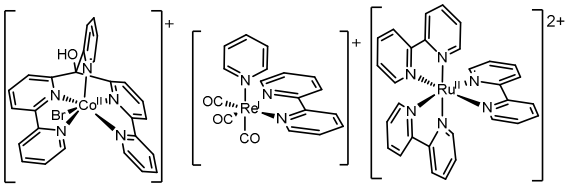
Ascorbate acts as reversible electron shuttle between tris(2-carboxyethyl) phosphine (TCEP) and Re^{I} or Ru^{II} photosensitizers. Oxidized ascorbate is recycled up to 50 times by the TCEP→TCEP=O redox process which enables 30'000 TONs/WRC in photocatalytic hydrogen production, thus exceeding the performance with pure ascorbate by far.

Solar energy is an alternative to fossil fuels due to its eco-friendliness and inexhaustibility: within 1 h, more solar energy reaches our planet than is totally used by mankind in one year, thus, even low conversion efficiencies would suffice to cover worldwide energy consumption.[1] Our energy demand, however, does not correlate with local availabilities of sunlight; hence new ways to store solar energy are crucial for meeting future energy demands.[2] Photo(electro)catalytic water splitting into H_2 and O_2 is a promising approach to store light in chemical bonds.[2-3] H_2 itself can be converted to liquid fuels via well established processes.[4] Due to the complexity of full water splitting systems, both half reactions are often investigated separately.[5] For the oxidative half reaction, sacrificial electron acceptors mimic the water reduction catalyst (WRC), whereas sacrificial electron donors (SEDs) are used to mimic the water oxidation catalyst (WOC) in the reductive half reaction, respectively. Only few SEDs are reported for water reduction - most common are ascorbic acid (AscOH), triethanolamine (TEOA) and trialkylamines.[5b, 6]

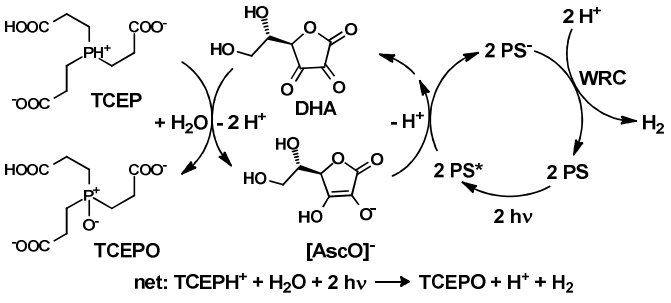
Under slightly basic reaction conditions, amines as SEDs are irreversibly converted to oxidized products which do not interfere with the catalytic cycle.[7] For the acidic pH range, ascorbic acid or ascorbate ($AscOH/AscO^-$) is a typically SED. Ascorbate is oxidized to dehydroascorbic acid (DHA)[8] which can be regenerated by reducing agents.[9] Therefore, the AscOH-DHA pair is a quasi reversible e^--donor. However, reversibility leads to e^--back transfer from reduced photosensitizer (PS^-) which then self inhibits photocatalysis at an early stage.[10] This effect is illustrated by photocatalytic experiments performed with WRC **1**, a Co^{II} complex with a pentadentate poly-pyridyl ligand (scheme 1). With $[Re(CO)_3(bpy)py]OTf$ (**2**) as PS and in 1 M AscOH/NaAscO as SED, TONs up to 11000 H_2/Co and TOFs 11000 H_2/Co/h could be achieved.[11] Although only a fraction of the SED was consumed, catalysis ceased due to self inhibition by DHA.[10, 12] An irreversible SED, active over a wide pH range and not limiting catalysis by e^--back transfer, will expand the scope of photocatalytic water reduction.



Scheme 1. Structures of catalysts used in this work; [CoBr(aPPy)]Br (**1**), $[Re(CO)_3(bpy)Py]OTf$ (**2**) and $[Ru(bpy)_3]Cl_2$ (**3**).

Recycling DHA with a 2nd SED would solve the self inhibition issue and make the AscOH/DHA couple not only a pure SED but a useful e^- relay. TCEP (tris(2-carboxyethyl) phosphine hydrochloride) is a strong, pH dependent reductant and known to reduce DHA to AscOH.[13] Upon reduction of DHA→AscOH, TCEP is oxidized to TCEPO which is less prone to e^--back transfer reactions than DHA.

We present a photocatalytic study with **1** as WRC, **2** or **3** as PS and TCEP as the ultimate SED. AscOH acts as an e^- relay, recycled up to 50 times until TCEP is fully consumed. Under optimized conditions, about 30'000 TONs per WRC **1** were achieved. The postulated electron transfer cycles are shown in scheme 2.



Scheme 2. Ascorbate coupled photocatalysis with TCEP as SED. According to the reported pKa values of TCEP,[14] at pH 4 two and at pH 5 all three carboxylic acid moieties are deprotonated. Potentials of the involved redox couples are shown in table SI3.

Photocatalytic experiments were typically performed in H_2O with 100 mM TCEP, 0.5 mM PS **2** or **3** and varying initial pH, [NaAscO] and [**1**] upon irradiation with a 385 nm (PS **2**) or

470 nm LED (PS **3**), respectively. H_2 evolution was continuously monitored by automated GC and TCEP→TCEPO conversion directly quantified by ^{31}P-NMR spectroscopy after catalysis. Although H_2 evolution was observed between pH 3 – 6, fastest conversions were obtained at pH 4 – 5 (table SI1). The overall reaction generates one additional H^+ per H_2 (Scheme 2). Both, TCEP and TCEPO act as buffer in this pH range (pK_a of TCEP: 2.9, 3.6, 4.3 and 7.6; TCEPO: 3.5, 4.2, 4.9).[14] Therefore, the pH decreased only marginally during catalysis (maximum 0.5 pH units).

In the absence of TCEP (0.1 M AscOH/NaAscO), H_2 formation rate was rather low and only 30 % (PS **2**), respectively 7 % (PS **3**), of NaAscO was converted to DHA and H_2 (as determined by GC, figure 1). Corresponding experiments with TCEP but without ascorbate exhibited even much lower H_2 evolution rates with PS **2** (figure 1 and SI1 and table SI4), whereas with **3** as PS, we found essentially no H_2 or TCEPO formation (figure 1 and SI2 and table SI5). This is consistent with the observation that **2*** is reductively quenched by TCEP, albeit at a 10^3 times lower rate ($1.15 \pm 0.04 \cdot 10^6$ $M^{-1}s^{-1}$, figure SI4) than by ascorbate,[10] whereas PS **3*** is not reduced at all.

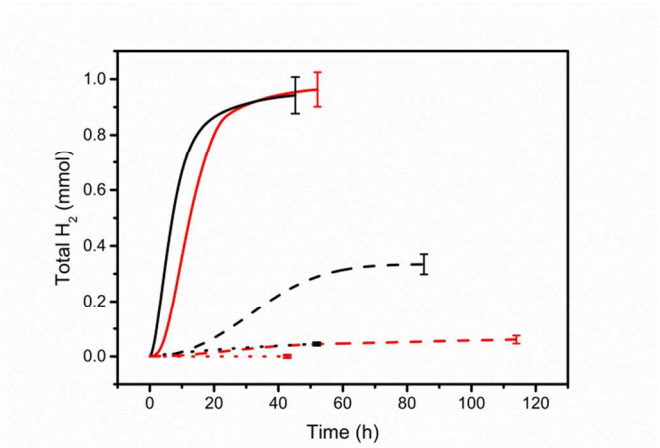


Figure 1. Comparison of H_2 evolution using either only ascorbate (dashed) or TCEP (dotted) based SED or TCEP/NaAscO couple (full line) in water with 100 µM **1** and 0.5 mM PS. Black line: 0.1 M TCEP, 25 mM NaAscO, PS **2**, pH 4, 100 % conversion (^{31}P-NMR); red line: 0.1 M TCEP, 100 mM NaAscO, PS **3**, pH 5, 100 % conversion (^{31}P-NMR); black dashed line: 0.1 M NaAscO/AscOH, PS **2**, pH 4, 30 % conversion (GC); red dashed line: 0.1 M NaAscO/AscOH, PS **3**, pH 5, 7 % conversion (GC); black dots: 0.1 M TCEP, 0.5 mM PS **2**, pH 4, 3% conversion (^{31}P-NMR); red dots: 0.1 M TCEP, 0.5 mM PS **3**, pH 5, no conversion (GC).

In comparison to photocatalytic reactions with the single SEDs, catalyses with a combination of TCEP and AscOH did not simply proceed as the sum of the individual, reductive quenchers but gave far higher reaction rates and total amounts of H_2 (figure 1). These results imply a synergistic interaction between TCEP and AscOH since TCEP alone is far too slow for the observed rates and AscOH alone would not result in the observed yields (figure 1, table SI4-5). In order to corroborate this hypothesis, we have studied the influence on the individual components on the course of photocatalysis.

Under the aforementioned conditions and at pH 4 – 5, TCEP was quantitatively converted to TCEPO when catalysis ceased. Full conversion was also achieved at pH 6, but reactions were significantly slower (table SI1). Wechtersbach et al. showed, that DHA is reduced to AscOH by TCEP between pH 1 – 7, at a pH dependent rate (k_1) of about 1 $M^{-1}s^{-1}$ between pH 4 and 5.[13a] Under our conditions, photocatalysis forms DHA at v_{max} ~$2 \cdot 10^{-6}$ Ms^{-1}, thus, a steady state concentration of ~20 µM DHA results at 0.1 M TCEP (equation 1).

_____ (1)

H_2 evolution rates and simultaneous conversion of TCEP are distinctly AscOH concentration dependent. For maximum rates and fast TCEP conversion, catalysis with PS **2** is limited by [$AscO^-$] up to ~10 mM whereas PS **3** reaches highest rates/conversion only at concentration >100 mM (figure 2, figure SI1-3, table SI4-5). We assign this effect to differences in the bimolecular reductive quenching rates of **3***→**3**$^-$ ($2 \cdot 10^7$ $M^{-1}s^{-1}$, pH 5),[15] which is more than two orders of magnitude slower than for **2***→**2**$^-$ ($2.6 \cdot 10^9$ $M^{-1}s^{-1}$, pH 4).[10] Although the lifetime of **3*** is longer than the one of **2** (630 ns and 120 ns, respectively), the calculated, maximum quenching yield for **2** exceeds the one of **3** substantially (figure 2).

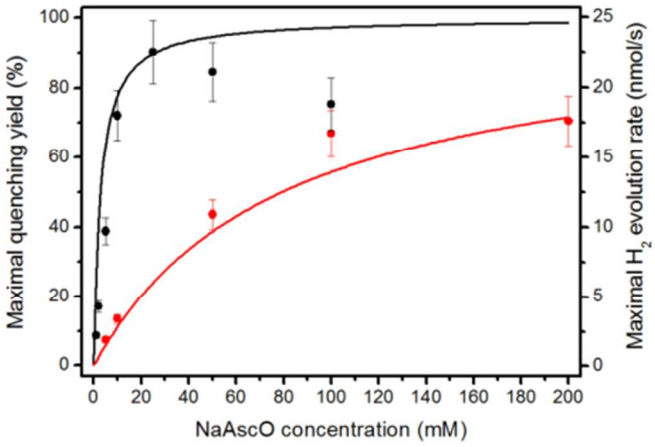


Figure 2. Calculated, maximum quenching yields by [$AscO^-$] for PS **2** (black line) and **3** (red line); experimental, maximum H_2 evolution rates (black dots: PS **2**, red dots: PS **3**) with 0.1 M TCEP, 0.1 mM **1** and 0.5 mM **2** or **3** at different [NaAscO] at pH 4 (PS **2**) or 5 (PS **3**). Maximum yields for reductive quenching are calculated according to $k_Q \cdot [Q]/(k_Q \cdot [Q] + \tau^{-1})$ (k_Q = bimolecular quench constant, [Q] quencher concentration, τ PS lifetime in the absence of quencher). Reaction rate vs. time are shown in figure SI1 and SI2 and reaction times over [NaAscO] in figure SI3.

H_2 evolution rates decreased whereas times to completion increased (figure 2 and SI3) at [$AscO^-$] <10 mM (PS **2**) and 100 mM (PS **3**), respectively, both in agreement with ascorbate being rate limiting at these concentrations. Above these limits, similar H_2 evolution rate courses and reaction times were observed (figure SI1-3 and table SI4-5). We note that even in slow reactions, TCEP was fully oxidized at 2 mM in [NaAscO] with **2** and at 5 mM with **3** respectively. Thus, ascorbate catalytically transferred electrons up to 50 times (50 H_2/NaAscO). Above concentrations at which ascorbate is rate limiting, TCEP→TCEPO conversion was complete in short times, making the combined system distinctly superior to the one with pure ascorbate as SED. We emphasize that TCEP suppresses self inhibition of photocatalysis by DHA which is continuously reduced to AscOH.

Exclusion of DHA as performance limiting parameter allows a better insight in WRC performance. Consequently, we determined TONs as a function of WRC concentration and conditions at which catalysis is not limited by [NaAscO] (0.1 M TCEP and 10 or 100 mM NaAscO with 0.5 mM PS **2** and **3** at pH 4 and 5, respectively). For reasons discussed below, we focused on PS **3** for these experiments. When lowering WRC **1**

concentrations from 100 to 1 µM, TONs and TOFs in Co increased from 1080 to 33'300 H_2/Co and from 70 to 5900 H_2/Co/h respectively (table SI2). Full conversion of TCEP was only achieved at [**1**] >25 µM. Still, >30'000 TONs at 1 µM in **1** are at least three times more as compared to ascorbate as sole SED.[11] For all WRC concentrations, absolute v_{max} for H_2 formation were about similar. At lower concentrations, the rates decreased faster which accounts for the not complete conversion of TCEP (figure SI5).

Replacing PS **3** by **2** gave qualitatively similar results but reaction rates dropped much faster. Hence, only comparably low TONs could be obtained, i.e. 2000 H_2/Co and 10 % TCEP conversion at 5 µM WRC. These differences indicate a PS stability limited performance. When lowering the WRC concentration, e^- - transfer from PS^- to WRC becomes rate limiting. Consequently, PS^- accumulates in solution.[10, 12] Since $\mathbf{2}^-$ and $\mathbf{3}^-$ are unstable in H_2O, they decompose in this WRC concentration range. As reported earlier, $\mathbf{2}^-$ is very prone for ligand substitution on the µsec to msec time scale.[16] LC-MS measurements after catalysis with PS **2** indicated the formation of $[Re(CO)_3(bpy)(TCEP)]^+$, $[Re(CO)_2(bpy)(TCEP)]^+$, $[Re(CO)_3(bpy)(TCEPO)]^+$ and $[Re(CO)_2(bpy)(MeOH)(H_2O)]^+$. Since *fac*-$Re(CO)_3$(diimine) phosphine complexes are known to undergo CO substitution upon irradiation,[17] the decomposition rate of **2** is probably significantly enhanced upon TCEP coordination which explains the lower TONs in Co as compared to reactions with **3**. Reduced PS **3** is also described as unstable in water under irradiation.[15] Indeed, HPLC analyses after photocatalysis with **3** and no or low amounts of WRC only showed undefined species. Obviously, **3** decomposes slower than **2** which accounts for higher TONs as found with **3**. Thus and to this end, the stability of the PS is limiting whereas the role of AscOH could be shifted from pure SED to an electron relay system.

Conclusions

Ascorbate, a frequently used, rapid and efficient sacrificial electron donor is oxidized during photocatalysis to DHA, an equally efficient self-inhibitor of the process. Regenerating AscOH from DHA by TCEP which, by itself, does not act as an SED, shifts the role of ascorbate from an SED to an electron relay. AscOH–DHA thus shuttles electrons from TCEP to the WRC cycle, allowing up to 50 TONs in ascorbate. Hence, self inhibition by e^- back transfer from PS^- to DHA can be excluded. In parallel, high H_2 evolution rates and total amounts of H_2 were achieved. With $[Ru(bpy)_3]^{2+}$ as PS, >30'000 TON_{Co} were obtained, supporting earlier statements for WRC **1** as being a stable and active WRC. In the presented system, the donor TCEP and the electron acceptor PS* are disconnected but communicate only via the ascorbate relay.

Notes and references

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† Electronic Supplementary Information (ESI) available: Standard procedures for catalytic reactions; pH, WRC, NaAscO and WRC rate dependency data. See DOI: 10.1039/c000000x/

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1. S. P. Sukhatme and J. K. Nayak, *Solar Energy Principle of Thermal Collection and Storage*, third ed. edn., Tata McGraw-Hill Publishing Company, 2007.
2. T. R. Cook, D. K. Dogutan, S. Y. Reece, Y. Surendranath, T. S. Teets and D. G. Nocera, *Chem Rev*, 2010, **110**, 6474-6502.
3. a)S. Chu and A. Majumdar, *Nature*, 2012, **488**, 294-303; b)G. F. Swiegers, D. R. MacFarlane, D. L. Officer, A. Ballantyne, D. Boskovic, J. Chen, G. C. Dismukes, G. P. Gardner, R. K. Hocking, P. F. Smith, L. Spiccia, P. Wagner, G. G. Wallace, B. Winther-Jensen and O. Winther-Jensen, *Aust J Chem*, 2012, **65**, 577-582; c)V. Balzani, A. Credi and M. Venturi, *ChemSusChem*, 2008, **1**, 26-58.
4. a)C. Higman and S. Tam, *Chem. Rev.*, 2013, **in press**, DOI: 10.1021/cr400202m; b)N. S. Lewis and D. G. Nocera, *P Natl Acad Sci USA*, 2006, **103**, 15729-15735.
5. a)T. S. Teets and D. G. Nocera, *Chem Commun*, 2011, **47**, 9268-9274; b)W. T. Eckenhoff and R. Eisenberg, *Dalton Trans.*, 2012, **41**, 13004-13021; c)D. G. Hetterscheid and J. N. Reek, *Angew. Chem.*, 2012, **51**, 9740-9747; d)M. Nippe, R. S. Khnayzer, J. A. Panetier, D. Z. Zee, B. S. Olaiya, M. Head-Gordon, C. J. Chang, F. N. Castellano and J. R. Long, *Chem. Sci.*, 2013, **4**, 3934; e)W. T. Eckenhoff, W. R. McNamara, P. Du and R. Eisenberg, *Biochim. Biophys. Acta, Bioenergetics*, 2013, **1827**, 958-973; f)V. Artero, M. Chavarot-Kerlidou and M. Fontecave, *Angew Chem Int Edit*, 2011, **50**, 7238-7266.
6. S. Losse, J. G. Vos and S. Rau, *Coordin Chem Rev*, 2010, **254**, 2492-2504.
7. B. Probst, A. Rodenberg, M. Guttentag, P. Hamm and R. Alberto, *Inorg. Chem.*, 2010, **49**, 6453-6460.
8. J. D. Deutsch, *J. Chromatogr. A*, 2000, **881** 299 -307.
9. J. B. Park, *Biochim. Biophys. Acta*, 2001, **1525**, 173-179.
10. M. Guttentag, A. Rodenberg, R. Kopelent, B. Probst, C. Buchwalder, M. Brandstätter, P. Hamm and R. Alberto, *Eur. J. Inorg. Chem.*, 2012, 59-64.
11. C. Bachmann, M. Guttentag, B. Spingler and R. Alberto, *Inorg. Chem.*, 2013, **52**, 6055−6061.
12. M. Guttentag, A. Rodenberg, C. Bachmann, A. Senn, P. Hamm and R. Alberto, *Dalton Trans.*, 2013, **42**, 334–337.
13. a)L. Wechtersbach and B. Cigić, *J. Biochem. Biophys. Methods*, 2007 **70**, 767–772; b)J. Lykkesfeldt, *Anal. Biochem.*, 2000, **282**, 89-93.
14. A. Krezel, R. Latajka, G. D. Bujacz and W. Bal, *Inorg. Chem.*, 2003, **42**, 1994-2003.
15. C. V. Krishnan, C. Creutz, D. Mahajan, H. A. Schwarz and N. Sutin, *Isr. J. Chem.*, 1982, **22**, 98-106.
16. B. Probst, M. Guttentag, A. Rodenberg, P. Hamm and R. Alberto, *Inorg. Chem.*, 2011, **50**, 3404-3412.
17. K. Koike, J. Tanabe, S. Toyama, H. Tsubaki, K. Sakamoto, J. R. Westwell, F. P. A. Johnson, H. Hori, H. Saitoh and O. Ishitani, *Inorg. Chem.*, 2000, **39**, 2777-2783.