

A renewable amine for photochemical reduction of CO₂

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Photochemical reduction of CO₂ (to produce formic acid) can be seen both as a method to produce a transportable hydrogen-based fuel and also to reduce levels of CO₂ in the atmosphere. However, an often overlooked necessity for photochemical CO₂ reduction is the need for a sacrificial electron donor, usually a tertiary amine. Here, we describe a new strategy for coupling the photochemical reduction of CO₂ to photochemical water splitting, and illustrate this with a prototype example. Instead of seeking to eliminate the use of an external reducing agent altogether, our alternative strategy makes the reducing agent recyclable. This has two potential advantages over the direct coupling of CO₂ reduction and water oxidation. First, it allows the two redox reactions to be carried out with existing chemistry, and second, it permits these reactions to be conducted under mutually incompatible conditions.

The demand for renewable energy sources that harvest solar energy is ever increasing¹. Of particular interest is the production of transportable fuels by artificial photosynthesis². Such technology might allow the energy from sunlight to be captured in parts of the world where food cannot be grown. An important step towards this goal, which has been studied by several chemists, is the photochemical reduction of carbon dioxide^{3,4}. The first isolatable reduction product of CO₂ is formic acid, HCO₂H, or its dehydration product, CO. The former is a useful liquid fuel for direct-oxidation fuel cells^{5,6}, and the latter can be used to generate hydrogen in the water–gas shift reaction⁷. Both processes regenerate CO₂, and so the complete cycle of reduction and reoxidation can be considered to be the utilization of CO₂ as a hydrogen storage material, for which many alternatives have been explored⁸.

There have been a number of recent impressive accomplishments in the photochemical reduction of CO₂, especially through the development of inorganic and organometallic photocatalysts⁴. For example, a mixture of Re^I(2,2'-bipyridyl)(CO)₃ complexes can be used with visible light to achieve quantum yields for CO production up to 0.59 (ref. 9). In another example, photocatalyst turnover numbers above 500 have been achieved using a mixture of *p*-terphenyl (PTP) and a cobalt macrocycle, in a system that affords moderate quantum yields of formate¹⁰.

However, all current schemes for the photochemical reduction of CO₂ consume at least one mole of sacrificial reductant (usually a tertiary amine) for every mole of CO₂ captured. This irreversible oxidation of the amine constitutes a significant economic and environmental disincentive for the exploitation of photochemical CO₂ reduction in the quest for sustainable energy sources. A key challenge⁴, which was recently identified in an international meeting on artificial photosynthesis (the White Paper resulting from this meeting was recently discussed in an editorial by Pike and Earis¹¹ and is provided in the supplementary information there), is to couple CO₂ reduction to photochemical water splitting, thereby achieving non-biomimetic photosynthesis of formic acid (or CO). However, elimination of the external reducing agent implies the direct coupling of two difficult redox reactions, which constitutes a formidable challenge, because the optimum conditions for the CO₂ reduction and water oxidation may be mutually incompatible.

For example, many of the existing CO₂ reduction schemes are carried out under non-aqueous conditions⁴. In this report, we outline and illustrate an alternative strategy. Instead of seeking to eliminate the external reductant, this new approach retains it, but seeks to make it recyclable by hydrogenation. This alternative strategy changes the research focus from the CO₂ reduction and water oxidation reactions themselves to the design of an optimal mediating reagent.

The role of the amine in photochemical reduction of CO₂ is first to provide an electron, thereby generating its radical cation. Thereafter, the reactions are complex and system-dependent, but the net effect is for the amine radical cation to lose a proton and a hydrogen atom. The intermediates generated in this sequence include iminium ions (by hydrogen atom loss from the α carbon of the amine side-chain), amino radicals (by proton loss from the α carbon) and enamines (by hydrogen loss from both α and β carbons)¹². Secondary reactions of these reactive species lead to the complex product mixtures typically observed from amine oxidations¹³.

Results

Our recent calculations¹⁴ have investigated ways in which the first-formed radical cation might be diverted to give an alkene product without generating any of the reactive intermediates listed above. The key step exploits a 1,5-hydrogen atom shift, first reported by Janovsky and colleagues¹⁵. Combining features of the amines studied computationally, the conformationally restricted tricyclic amine **1** was designed (Fig. 1). In addition to allowing the 1,5-hydrogen migration (**2** \rightarrow **3** in Fig. 1) to occur via an essentially strain-free transition structure, the tricyclic design of amine **1** also blocks the formation of any of the undesired reactive intermediates in the rings, because of the bridgehead location of the α hydrogens. In principle, the hydrogens on the N–CH₃ could become involved, but preliminary mechanistic work on related amines suggests that they should be of low reactivity. Second-generation amines could replace this methyl by a tertiary alkyl group, if necessary.

A derivative (**9**), of amine **1** was prepared from ketone **7**, itself available in two steps from commercial 2-chlorocyclohexanone and *N*-(*tert*-butoxycarbonyl)pyrrole¹⁶. The methoxy group in amine **9** was left, because fully reducing the carbonyl group in ketone **7** proved troublesome.

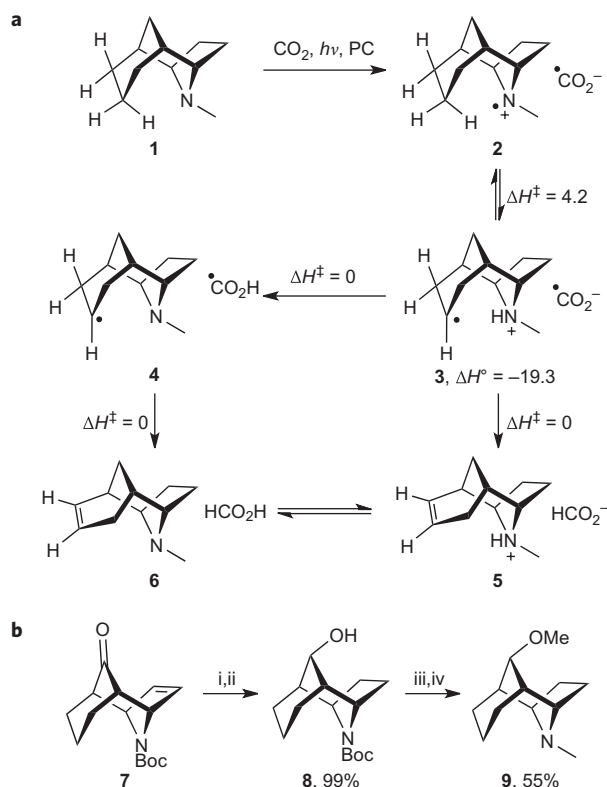


Figure 1 | Design of a renewable amine for photochemical reduction of CO_2 . **a**, Calculated mechanism for photochemical CO_2 reduction by amine **1** based on previous work¹². Enthalpies were calculated at 298 K, using corrected¹² B3LYP/6-31 + G(d,p) with a polarizable continuum model for CH_3CN , and are given in kJ mol^{-1} . The hydrogen atom transfers $3 + \text{CO}_2 \rightarrow 5 + \text{HCO}_2^-$ and $4 + \text{HCO}_2\text{H} \rightarrow 6 + \text{HCO}_2\text{H}$ were each found to be barrierless and highly exothermic. PC, photocatalyst. **b**, Synthesis of amine **9**, an accessible derivative of **1**. Reagents: (i) H_2 , Pd/C, EtOH; (ii) NaBH_4 , EtOH; (iii) KH, DMF then Me_2SO_4 ; (iv) LiAlH_4 , THF. Boc, *tert*-butyloxycarbonyl; DMF, *N,N*-dimethylformamide; THF, tetrahydrofuran.

Photochemical studies on CO_2 reduction by amine **9** were performed in acetonitrile- d_3 (CD_3CN) or *N,N*-dimethylformamide- d_7 ($\text{DMF-}d_7$), using the conditions reported by Matsuoka and colleagues¹⁷. The photolysate was analysed directly by nuclear magnetic resonance (NMR) spectroscopy and gas chromatography mass spectrometry (GCMS). After irradiation of amine **9** at 254 nm with the photocatalyst PTP and CO_2 in $\text{DMF-}d_7$, the ^1H NMR spectrum showed the presence of formate, produced with an apparent quantum yield similar to that for triethylamine under the same conditions. The ^1H NMR spectrum of the photolysate also showed signals tentatively ascribed to the expected oxidation product (**10**) of the amine. Because separation of this product from amine **9** proved difficult, an independent synthesis of compound **10** was undertaken. It was made from commercial *N*-tosylpyrrole **12** plus enamine **11**, available in four steps from 4-methoxyphenol¹⁸ (Fig. 2). This synthesis established, indeed, that alkene **10** was produced during the photochemical reduction of CO_2 with amine **9**. It was also confirmed that compound **10** could be converted back to amine **9** by hydrogenation with a palladium-on-carbon (Pd/C) catalyst in ethyl acetate (EtOAc) solvent. This sequence therefore establishes, we believe for the first time, that an amine reducing agent can be regenerated by hydrogenation after use in the photochemical reduction of CO_2 .

An unexpected feature of alkene **10** merits some discussion. Attempted hydrogenation of **10** with Pd/C in ethanol did not afford **9**. Instead, the tetracyclic ammonium ion **17** was formed

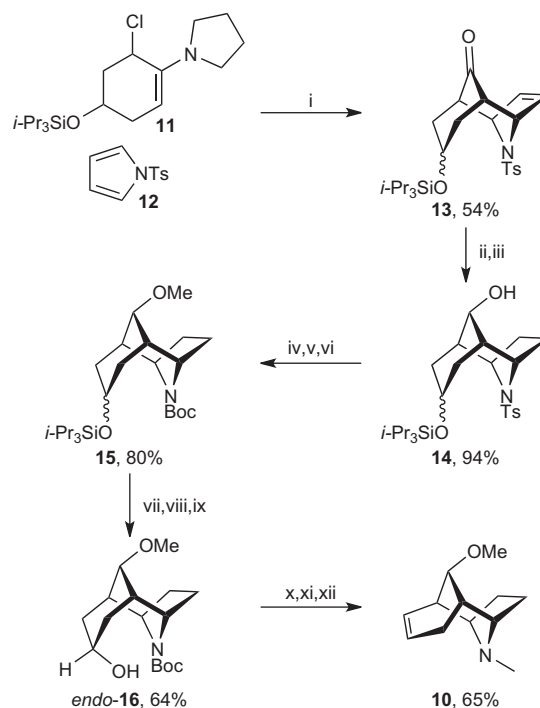


Figure 2 | Independent synthesis of alkene **10.** Reagents: (i) AgBF_4 , CH_2Cl_2 then NaOH, MeOH/ H_2O ; (ii) H_2 , Pd/C, EtOH; (iii) NaBH_4 , EtOH; (iv) lithium di-*tert*-butylbiphenylide, THF; (v) Boc₂O, THF; (vi) KH, DMF, then Me_2SO_4 ; (vii) $\text{Bu}_4\text{N}^+ \text{F}^-$, THF; (viii) pyridinium chlorochromate, CH_2Cl_2 ; (ix) NaBH_4 , EtOH; (x) MeSO_2Cl , Et_3N , CH_2Cl_2 ; (xi) KO^tBu , dimethylsulfoxide (DMSO); (xii) LiAlH_4 , THF. Ts, *p*-toluenesulfonyl.

(Fig. 3). After transfer to CDCl_3 for NMR analysis, the counterion X^- could be shown (by silver nitrate test) to be Cl^- , but its original identity proved harder to determine. Obviously, structure **17** is a formal Brønsted-acid addition product of **10**, not a reduction product, and indeed experiments revealed that no H_2 was required for its formation. More surprisingly, addition of a strong Brønsted acid, $\text{F}_3\text{CCO}_2\text{H}$, to **10** in CDCl_3 , CD_3CN or D_2O resulted only in N protonation. Only a trace of **17** could be detected after 10 days at room temperature. Treatment of **17** ($\text{X}^- = \text{Cl}^-$) with potassium *tert*-butoxide in dimethylsulfoxide (DMSO) resulted in near quantitative conversion back to **10**. These observations suggest that the

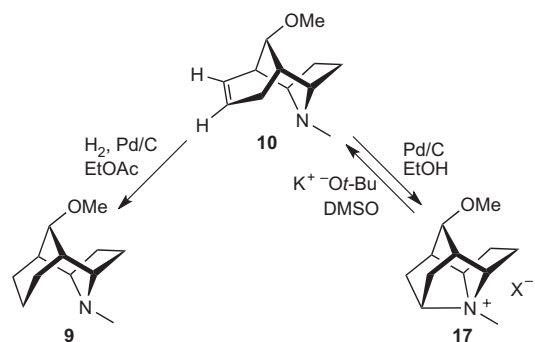


Figure 3 | Regeneration of amine **9 by hydrogenation of alkene **10**, and an unexpected side reaction.** Treatment of alkene **10** with hydrogen in ethanol solvent in the presence of Pd/C catalyst did not result in formation of the saturated amine **9**. Analysis indicates the tetracyclic ammonium ion **17** was formed and it was then shown that no hydrogen was required for its formation. Formation of **17** was reversible using potassium *tert*-butoxide in DMSO. Hydrogenation in ethyl acetate solution, however, was successful in regenerating the amine **9**.

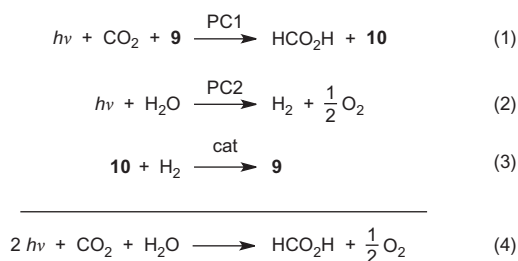


Figure 4 | Illustration of the general strategy for coupling of CO₂ reduction and water splitting. PC1 and PC2, photocatalysts; cat, hydrogenation catalyst.

equilibrium between N-protonated **10** and **17** is strongly solvent and counterion dependent, and that under some circumstances there can be a substantial barrier to the formation of **17**. Density functional theory (DFT) calculations support the conclusion about counterion dependence. At 298 K in acetonitrile, calculations suggest an equilibrium constant of $\sim 1 \times 10^9$ in favour of the tetracyclic ion **17** when $\text{X}^- = \text{Cl}^-$, but $\sim 1 \times 10^{10}$ in favour of the alkene **10** + HX when $\text{X}^- = \text{HO}^-$. These observations have potential utility in the principal goals of the project, because ion **17** appears to have better long-term stability than alkene **10** to prolonged photolysis, and so finding conditions for the photochemical reduction of CO₂ that are also conducive to the formation of **17** might improve the efficiency with which the amine could be regenerated. These possibilities are under investigation.

Discussion

The general strategy that has been discussed in this report can be summarized in the equations of Fig. 4. By demonstrating that amine **9** can act as the reducing agent XH₂ in equation (1) (Fig. 4), and by further demonstrating that it can be regenerated from its oxidation product, **10**, by hydrogenation, as in equation (3) (Fig. 4), we have proven, we believe for the first time, that this general strategy is feasible. However, we do not pretend that this prototype sequence is optimal, or that this alternative to the direct coupling of CO₂ reduction and water oxidation is without challenges of its own. Among those, obvious candidates for attention are the engineering issues associated with the separation of X from the reaction mixture in equation (1) and of XH₂ from the regeneration reaction, equation (3). This could perhaps be facilitated by attachment of X/XH₂ to a polymer, but other possibilities exist. In addition, the cost and turnover number for the X/XH₂ pair will be important issues to address. Finally, we note that electrolysis of water can be combined with the direct *in situ* hydrogenation of organic substrates¹⁹. If the same could be accomplished in a photoelectrochemical cell used for water splitting, then the second and third reactions of Fig. 4 could perhaps be collapsed into a single transformation, with a likely improvement in efficiency. Here, too, the separation of the CO₂ reduction and water-splitting reactions would be advantageous, because the electrochemical hydrogenation requires low-pH conditions¹⁸, under which an amine such as **9** would be fully protonated, and hence incapable of participating in CO₂ reduction.

Although amine **9** has so far been tested only with the PTP photocatalyst, mechanistic studies on other photocatalysts suggest that they too involve the initial generation of a radical cation from the amine reducing agent, followed by net hydrogen atom and proton loss from the resulting radical cation^{4,8,20}. Consequently, one might anticipate that amine **9**, or analogues operating on a similar principle, could have general utility in the photochemical reduction of CO₂, including those operating with visible light.

Methods

All synthetic, photochemical and computational methods are included in the Supplementary Information.

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References

- Mitchell, J. F. B., Lowe, J., Wood, R. A. & Vellinga, M. Extreme events due to human-induced climate change. *Philos. Trans. R. Soc. A* **364**, 2117–2133 (2006).
- Goldemberg, J. The promise of clean energy. *Energy Policy* **34**, 2185–2190 (2006).
- Hawecker, J., Lehn, J. M. & Ziessel, R. Electrocatalytic reduction of carbon dioxide at illuminated p-type silicon semiconducting electrodes. *Chem. Commun.* 536–538 (1983).
- Morris, A. J., Meyer, G. J. & Fujita, E. Molecular approaches to the photocatalytic reduction of carbon dioxide for solar fuels. *Acc. Chem. Res.* **42**, 1983–1994 (2009).
- Ha, S., Dunbar, Z. & Masel, R. I. Characterization of a high performing passive direct formic acid fuel cell. *J. Power Sources* **158**, 129–136 (2006).
- Casado-Rivera, E. *et al.* Electrocatalytic activity of ordered intermetallic phases for fuel cell applications. *J. Am. Chem. Soc.* **126**, 4043–4049 (2004).
- Jacobs, G. & Davis, B. H. Low temperature water-gas shift catalysts. *Catalysis* **20**, 122–285 (2007).
- Graetz, J. New approaches to hydrogen storage. *Chem. Soc. Rev.* **38**, 73–82 (2009).
- Takeda, H., Koike, K., Inoue, H. & Ishitani, O. Development of an efficient photocatalytic system for CO₂ reduction using rhenium(I) complexes based on mechanistic studies. *J. Am. Chem. Soc.* **130**, 2023–2031 (2008).
- Matsuoka, S. *et al.* Efficient and selective electron mediation of cobalt complexes with cyclam and related macrocycles in the p-terphenyl-catalyzed photoreduction of CO₂. *J. Am. Chem. Soc.* **115**, 601–609 (1993).
- Pike, R. & Earis, P. Powering the world with sunlight. *Energy Environ. Sci.* **3**, 173 (2010).
- Carpenter, B. K. Computational study of CO₂ reduction by amines. *J. Phys. Chem. A* **111**, 3719–3726 (2007).
- Cohen, S. G., Parola, A. & Parsons, G. H. Jr. Photoreduction by amines. *Chem. Rev.* **73**, 141–161 (1973).
- Richardson, R. D. & Carpenter, B. K. A computational study of remote C-H activation by amine radical cations: implications for the photochemical reduction of carbon dioxide. *J. Am. Chem. Soc.* **130**, 3169–3180 (2008).
- Janovsky, I., Knolle, W., Naumov, S. & Williams, F. EPR studies of amine radical cations. Part 1: thermal and photoinduced rearrangements of n-alkylamine radical cations to their distonic forms in low-temperature freon matrices. *Chem. Eur. J.* **10**, 5524–5534 (2004).
- Jin, S.-J., Choi, J.-R., Oh, J., Lee, D. & Cha, J. K. [4 + 3] cycloadditions of cyclic oxyallyls and cyclic 1,3-dienes. *J. Am. Chem. Soc.* **117**, 10914–10921 (1995).
- Matsuoka, S. *et al.* Photocatalysis of oligo(p-phenylenes). Photochemical reduction of carbon dioxide with triethylamine. *J. Phys. Chem.* **96**, 4437–4442 (1992).
- Lee, J. *et al.* Fragmentation of alkoxy radicals and oxidative elimination of alicyclic iodides. *J. Org. Chem.* **59**, 6955–6964 (1994).
- Itoh, N., Xu, W. C., Hara, S. & Sakaki, K. Electrochemical coupling of benzene hydrogenation and water electrolysis. *Catal. Today* **56**, 307–314 (2000).
- Whitten, D. G. Photoinduced electron transfer reactions of metal complexes in solution. *Acc. Chem. Res.* **13**, 83–90 (1980).

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Author contributions

B.K.C. directed and coordinated the project. E.J.H. and R.D.R. developed the synthesis of amine **9** and performed the preliminary photochemical studies. R.D.R. and B.K.C. wrote the paper and performed the DFT calculations. R.D.R. developed the authentic synthesis of alkene **10**, performed the final photochemical studies and studied the hydrogenation and formation of **17**. All authors commented on the paper.

Additional information

The authors declare no competing financial interests. Supplementary information and chemical compound information accompany this paper at www.nature.com/naturechemistry. Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>. Correspondence and requests for materials should be addressed to B.K.C.