Coordination Chemistry Reviews 254 (2010) 2472–2482

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Toward more efficient photochemical CO_2 reduction: Use of $scCO_2$ or photogenerated hydrides

Mark D. Doherty, David C. Grills, James T. Muckerman, Dmitry E. Polyansky, Etsuko Fujita*

Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000, USA

Contents

A R T I C L E I N F O

Article history:
Received 25 September 2009
Accepted 6 December 2009
Available online 8 January 2010

Keywords:
Carbon dioxide reduction
Small molecule activation
Photocatalysis
Renewable hydride donors
Supercritical CO_2
NADH-model ligands

A B S T R A C T

Rhenium(I) and ruthenium(II) complexes have been successfully used for photochemical CO_2 reduction to CO or formate. However, a typical turnover frequency for such reactions is <20 h^{-1} and the formation of reduced species beyond CO or formate is very limited. In the case of the rhenium(I) bipyridyl tricarbonyl system, the key intermediate has been shown to decay with a first-order dependence on $[CO_2]$ to produce CO, which is the rate-determining step. The limited concentration of dissolved CO_2 in organic solvents results in extremely slow CO_2 reduction. To improve the reaction rate, we prepared new CO_2-soluble rhenium(I) bipyridine complexes bearing fluorinated alkyl ligands and investigated their photophysical properties in CH_3CN and supercritical CO_2. We also investigated the properties of a metal complex with an NAD^+ model ligand, $[Ru(bpy)_2(pbn)]^{2+}$ (bpy = 2,2′-bipyridine, pbn = 2-(2-pyridyl)-benzo[*b*]-1,5-naphthyridine), and prepared the corresponding NADH-like complex $[Ru(bpy)_2(pbnHH)]^{2+}$ upon MLCT excitation followed by reductive quenching. This species can be used as a renewable hydride donor. The electrochemical and photochemical properties, and the reactivity of these species toward CO_2 reduction were investigated.

1. Introduction

There is currently a considerable research effort into the development of efficient methods for Carbon Capture and Storage (CCS), in which CO_2 from industrial and energy-related sources would be captured and stored indefinitely. This has been prompted by rapidly rising atmospheric CO_2 levels (currently at ∼386 ppm [1]), which threaten to cause catastrophic environmental damage through global warming [2–4]. However, an attractive alternative to storing the captured CO_2 would be to make use of it as a feedstock for the production of clean fuels, such as methanol and methane, and/or fine chemicals. Being the final product of combustion, CO_2 is a thermodynamically stable and inert molecule. Thus, its conversion into higher-energy reduced forms requires the input of large amounts of energy and catalysts to mediate the reactions. Therefore, if such a process is to become economically viable, a renewable source of energy is essential. One of the most promising strategies would be to make use of solar energy in so-called 'artificial photosynthetic' processes, in which simple chemical transformations, inspired by the more complex natural photosystems, convert CO_2 into reduced forms. This type of photochemical CO_2 reduction has been the subject of intense research for a number of years now. As can be seen in Table 1, the electrochemical potential for the direct one-electron reduction of CO_2 to $CO_2^{\bullet-}$ is −1.90 V vs. NHE, making this a highly unfavorable process [5]. Large kinetic overpotentials are also observed for this electrochemical reduction due to the barrier arising from the conversion of linear CO_2 into bent $CO_2^{\bullet-}$. In contrast, proton-assisted multielectron processes, although often kinetically challenging, are much more thermodynamically favorable (see Table 1) [6]. Though stoichiometric conversions of CO_2 have been reported, many of which are currently used in industry, this paper will focus on photocatalytic reactions using transition-metal complexes as catalysts.

---

* Corresponding author at: Chemistry Department, Brookhaven National Laboratory, Bldg 555, Upton, NY 11973-5000, USA. Tel.: +1 631 344 4356.
E-mail address: fujita@bnl.gov (E. Fujita).

0010-8545/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2009.12.013

Table 1
Reduction potentials for various CO_2 reduction reactions in aqueous solution at pH 7 vs. NHE. All other solutes at 1 M.

Reaction	$E^{0'}$ (V)
$CO_2 + e^- \rightarrow CO_2^{\bullet -}$	−1.90
$CO_2 + H^+ + 2e^- \rightarrow HCO_2^-$	−0.49
$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$	−0.61
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.53
$CO_2 + 4H^+ + 4e^- \rightarrow C + 2H_2O$	−0.20
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	−0.48
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	−0.38
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	−0.24

The use of metal-based catalysts has several advantages. For example, through careful ligand and metal modifications, the absorption spectrum of the catalyst can be tuned to capture visible light within the solar spectrum. Furthermore, upon absorption of light these complexes often exhibit long-lived charge-separated excited states that can be efficiently coupled with multielectron-redox processes to activate and reduce CO_2. Thus, the use of such catalysts avoids high-energy intermediates and facilitates the coupling of electron transfer to bond-forming reactions, generally through an initial coordination of a CO_2 molecule to a vacant coordination site of the reduced form of the catalyst. The metal complexes may act as photosensitizers, working in combination with secondary electron relay catalysts to couple the photon energy to the chemical reduction, or they may be catalysts that are sensitized by organic or inorganic photosensitizers, or they can combine both functions into a single species.

Researchers in this field have achieved the efficient coupling of light absorption and charge separation with dark catalytic reactions to produce CO and formate under a variety of conditions (Table 2) [4,6]. The photocatalytic CO_2 reduction systems listed in Table 2 can be grouped into four general categories: (1) $Ru(bpy)_3^{2+}$ type complexes as a photosensitizer with a metal colloid or metal complex (including $Ru(bpy)_3^{2+}$) as a catalyst; (2) organic photosensitizers with a metal complex as a catalyst; (3) metal porphyrin complexes as both a photosensitizer and a catalyst; and (4) *fac*-$ReX(bpy)(CO)_3$ type complexes as both a photosensitizer and a catalyst. We are especially interested in catalyst systems belonging to group (4) which have recently been reported to be capable of achieving quantum yields for CO formation of 59% using a dual $Re(bipyridyl)(CO)_3X$-type photosensitizer-catalyst system [7]. However, typical turnover frequencies and turnover numbers for CO formation are less than $20\,h^{-1}$ and ∼250, respectively, owing to the nature of the extremely stable CO_2 molecule and low stability of catalysts and/or photosensitizers. There exist even more formidable challenges for CO_2 utilization. For example, in order to use the current infrastructure, a liquid fuel, e.g., methanol, has to be photochemically produced from CO_2. Furthermore, we need to couple reductive (*i.e.*, CO_2 reduction) and oxidative (*i.e.*, water oxidation) half-reactions to eliminate the use of a sacrificial electron donor. In this review, we will discuss molecular approaches toward: (1) more efficient photochemical reduction of CO_2 using CO_2-soluble tricarbonyl rhenium complexes with bpy-type ligands in supercritical CO_2 and (2) CO_2 reduction beyond CO using photogenerated renewable hydride donors.

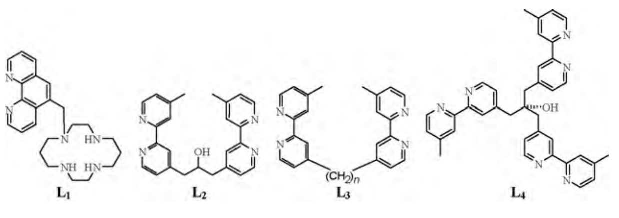

Chart 1. Structures of ligands $\mathbf{L_1}$–$\mathbf{L_4}$.

2. Photochemical CO_2 reduction using tricarbonyl rhenium(I) complexes with 2,2′-bipyridine (bpy) or similar ligands

Complexes of the general formula *fac*-$ReX(\alpha\text{-diimine})(CO)_3{}^n$ (α-diimine = bpy or substituted bpy and $n = 0$, X = Cl^-, Br^-; $n = +1$, X = PR_3, solvent, etc.) have been shown to effectively catalyze the reduction of CO_2 to CO in the presence of sacrificial electron donors, under the appropriate photochemical conditions. These complexes typically possess intense metal-to-ligand charge transfer (MLCT) absorption bands between 340 and 500 nm depending on the ligand set and solvent [43,44]. Initial light absorption produces a ^{3}MLCT excited state, which is emissive in solution with excited state lifetimes ranging from 27 ns (X = Cl^-, α-diimine = bpy) [45] to 1034 ns (X = $P(OEt)_3$, α-diimine = bpy) [46] in CH_3CN. Quantum yields for CO formation using these complexes have been reported, ranging from $\Phi_{CO} = 0.14$ (X = Cl^-, α-diimine = bpy) [27,28,43] to $\Phi_{CO} = 0.38$ (X = $P(OEt)_3$, α-diimine = bpy) [33], with the highest value of $\Phi_{CO} = 0.59$ reported for a dual component photosensitizer-catalyst system consisting of a 25:1 ratio of [*fac*-$(4,4'\text{-}(MeO)_2\text{-bpy})(CO)_3Re\{P(OEt)_3\}][PF_6]$:[*fac*-$(bpy)(CO)_3Re(CH_3CN)][PF_6]$ [7].

Mechanistic studies of electrocatalytic CO_2 reduction with these rhenium complexes have led to the proposal of simultaneous one- and two-electron pathways leading to CO formation with a current efficiency of 98% [47,48]. Using *fac*-$ReCl(bpy)(CO)_3$ as an example, the first step involves the generation of a one-electron reduced (OER) species [*fac*-$ReCl(bpy)(CO)_3]^-$ (see Fig. 1) at −1.5 V vs. SCE in CO_2-saturated CH_3CN [48]. Loss of Cl^- from this OER species is slow, producing a $17e^-$ metal-centered radical [*i.e.*, *fac*-$Re^\bullet(bpy)(CO)_3$], which in polar solvents (CH_3CN, THF, DMF, etc.) is rapidly trapped by a solvent molecule to form the ligand-centered radical, [*fac*-$Re^I(bpy^{\bullet -})(CO)_3(solv)$]. In the one-electron pathway [47,48], it is proposed that solvent is replaced by CO_2 and subsequent reductive disproportionation with another CO_2 molecule forms CO and $CO_3{}^{2-}$. For the two-electron pathway [47] reduction of the solvent-coordinated radical at −1.8 V vs. SCE in CH_3CN results in the formation of a five coordinate $18e^-$ metal-based anion, [*fac*-$Re(bpy)(CO)_3]^-$. Subsequent coordination of CO_2 followed by reaction with additional CO_2 as an oxide acceptor (Fig. 1) produces CO and $CO_3{}^{2-}$. After CO formation, both one- and two-electron pathways form a cationic solvent-coordinated species, [*fac*-$Re(bpy)(CO)_3(solv)]^+$ which upon reduction regenerates the solvent-coordinated ligand-centered radical species, closing the catalytic cycle. While the OER and [*fac*-$Re(bpy)(CO)_3]^-$ have been observed using infrared spectroelectrochemical techniques [47], neither of the proposed CO_2 adducts, [*fac*-$Re(bpy)(CO)_3(CO_2)]^\bullet$ or [*fac*-$Re(bpy)(CO)_3(CO_2)]^-$ have been observed during catalysis. Very little is known about the C═O bond cleavage steps involved in CO formation by the one- or two-electron pathways, however several species including metallocarboxylate and metallocarboxylic acid complexes have been postulated as intermediates [47–49].

Similar one- and two-electron mechanistic pathways have been proposed for the photochemical reduction of CO_2 using these rhenium catalysts based on a number of reactions which have been observed spectroscopically. Initial photoexcitation of *fac*-$ReCl(dmb)(CO)_3$ (dmb = 4,4′-dimethyl-2,2′-bipyridine) followed by reductive quenching by a tertiary amine (NEt_3 (TEA) or $N(CH_2CH_2OH)_3$ (TEOA)) produces an analogous OER species (*vide supra*) [50]. Rapid solvation following chloride