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Rapid Transfer of Hydride Ion from a Ruthenium Complex to C_1 Species in Water

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Water is recognized as a desirable solvent for catalysis[1,2] and as a promising raw material for solar generation of fuels;[3] however, relatively few kinetics and mechanism studies of C_1 reduction reactions[4] in aqueous media have been reported. The observation of Konno et al.[5] that high solvent acceptor number[6] (AN) enhances the rate of hydride transfer from Ru(terpy)(bpy)H^+ (RuH^+, terpy = 2,2′,6′,2″-terpyridine; bpy = 2,2′-bipyridine, Chart 1) to carbon dioxide in organic solvents has led us to characterize this reaction in water. We find that solvent water (AN = 55) accelerates the CO_2 reaction rate by more than 4 orders of magnitude compared to acetonitrile (AN = 18.9) and that water also promotes the related reductions of C_1 species carbon monoxide and formaldehyde by RuH^+.

The lowest energy electronic absorption of RuH^+, a Ru(II)-to-terpy charge transfer at 500 nm in water, shifts to shorter wavelength upon hydride transfer to C_1. The kinetics of the hydride-transfer reactions were followed by UV−vis spectroscopy, with both CO_2 and CH_2O requiring stopped-flow methods. All exhibited second-order rate laws, $-d[RuH^+]/dt = k_A[RuH^+][A]$ M s^{-1} where A is the hydride acceptor, CO_2 (see Figure 1), CO, or CH_2O.[7]

Product solutions were characterized by electrospray ionization mass spectrometry (ESI-MS), and assignments were confirmed by comparison with authentic samples prepared by other methods.[7] With CO_2 reactant, product $m/z = 536$ is assigned to ^{102}Ru(terpy)(bpy)[OCH(O)]$^+$. For CO, the $m/z = 351.6$ peak is assigned as ^{102}Ru(terpy)(bpy)($OCH_2(OH)$)[PF_6](H_3O)$^{2+}$ ($z = 2$, $m = 703$). With formaldehyde as reactant, $m/z = 522$ is ^{102}Ru(terpy)(bpy)(OCH_3)$^+$. Scheme 1 summarizes the reaction sequence.

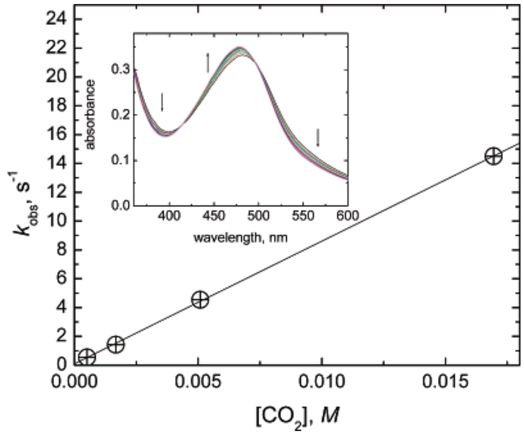


Figure 1. The pseudo-first-order rate constant for reaction of Ru(terpy)(bpy)H^+ with CO_2 at pH 5.8 as a function of CO_2 concentration. Inset: Scans taken every 500 ms with 1.5% saturated CO_2 (0.45 mM, first point).

Chart 1

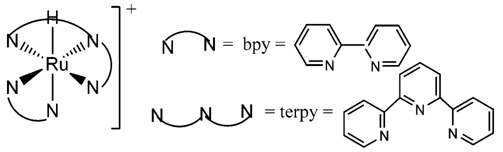
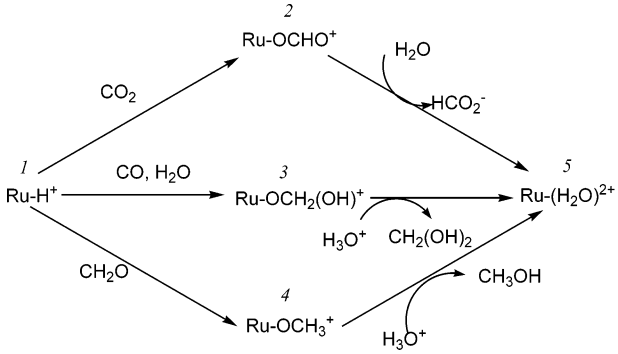


Table 1. Rate Constants and Products for the Hydride Transfer to Acceptor A

parameter	A		
	CO_2	CO	CH_2O
k_A, M^{-1} s^{-1} [a]	8.5×10^2	0.7	$\sim 1 \times 10^6$
λ_{max}, nm [b]	490	487	486
m/z product [c]	536 (100%)	351.6 (85%)	522 (30%) [d]
k_{aq}, s^{-1}	0.4×10^{-3} [e]	1.4×10^{-4} [e]	8.8×10^{-4} [f]

[a] Rate constant for hydride transfer to A (Scheme 1). [b] Position of lowest energy MLCT band of hydride adduct of A. [c] Value in parenthesis is relative intensity at its maximum (usually first trace). [d] The product methanol complex manifested as an intense peak at $m/z = 523$ only when the collision energy was reduced to 25%. [e] Rate of aquation at pH 5.3. [f] Rate of aquation in water, no buffer added.

Scheme 1



In contrast to previous studies of hydride transfer to free[2] or metal-bound C_1 species such as $Ru^{II}(bpy)_2(CO)(C_1)$,[8−11] for each hydride-transfer reaction studied here the initial product implicated is the O-bonded hydride adduct: formate ion $RuOCHO^+$ (2), formaldehyde hydrate $RuOCH_2(OH)^+$ (3), or methanol $RuOCH_3^+$ (4). This assignment is consistent with the ESI MS, UV−vis spectrum, comparison with known samples, and the relatively rapid transformation to Ru−OH_2^{2+} (λ_{max} 477, pK_a 10).[12] Results are summarized in Table 1. The importance of the Lewis acidity of the anhydride or keto form of the C_1 acceptor to its ability to accept hydride ion is striking. For CO_2, a pH-jump experiment[13,14] established that reaction of RuH^+ with CO_2 is >50 times greater than with HCO_3^-. For CO, reaction with its hydrate, formate ion, is $<10^{-5}$ M^{-1} s^{-1}, at least one-million times slower than the reaction with CO. Similarly for formaldehyde, the minor species H_2CO[15,16] was at least 10^5 times more reactive than its dominant hydrate form.

We bracket the hydricity[17] of this Ru(II) hydride using our kinetic data. The intercept of the plot of k_{obs} versus [CO_2] is 0.1 s^{-1}, and the slope is 8.5×10^2 M^{-1} s^{-1}. Then the rate constant for the reverse

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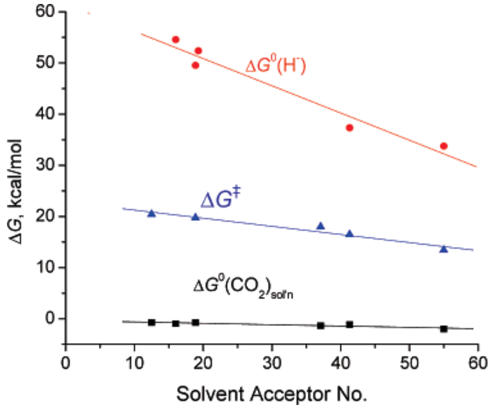
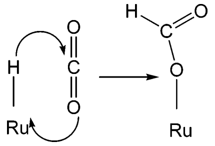


Figure 2. Free energies of hydride-ion formation ($\Delta G^0(H^-)$) (circles),[19] free energy of activation $\Delta G^‡$ for hydride transfer from RuH^+ to CO_2 (triangles),[5] and ($\Delta G^0(CO_2)_{soln}$), the free-energy of solution[5] of CO_2 (squares), as a function of solvent acceptor number.[6]

reaction is $\leq 0.1\ s^{-1}$, and $K_{A,12}$ for the hydride transfer (from the ratio of forward and reverse constants) is $\geq 10^4\ M^{-1}$ and $\Delta G^0 \leq -5$ kcal/mol. Since the hydricity of formate in water is 23 kcal/mol[18] (based on $pK_a(H_2) = 22$[19] rather than the commonly used, earlier value 31), the hydricity of Ru(terpy)(bpy)H$^+$ in water is ≤ 18 kcal/mol.

As discussed previously[5,20] for reaction of CO_2 with RuH^+ and Re(bpy)(CO)$_3$H, these reactions involve hydride transfer via transition states (Scheme 2) for CO_2.

Scheme 2



The reactions cannot involve Ru binding of O, followed by transfer of H^-, since substitution reactions at the Ru(II) center are many orders of magnitude too slow[21] (for binding of acetonitrile, $k = 0.3 \times 10^{-4}\ M^{-1}\ s^{-1}$)[18] to account for the observed rates.

On the basis of the work presented, it is evident that water is an excellent solvent for the hydride transfer to the free C_1 acceptors. It is of great interest to understand the basis of this reactivity enhancement, which is much greater than expected from dielectric continuum considerations.[5,20] We compare the effect of solvent acceptor number on thermodynamic and kinetic parameters in Figure 2.

Acceptor number reflects the electrophilic properties of the solvent; with increasing AN, the negative charge on the hydride ligand is increasingly stabilized. The trend observed here for $\Delta G^0(H^-)$ has also been found for chloride ion.[6] The plot in Figure 2 strongly suggests that the thermodynamics of formation of the hydride ion is responsible for the exceptional solvent sensitivity of the hydride-transfer rate to solvent acceptor number and encourages us to explore the scope of this reactivity enhancement in future experiments with other metal-hydride donors and both metal-bound and free hydride acceptors.

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Supporting Information Available: Experimental details, kinetics and products for reaction with CO_2, CO, and CH_2O, the hydricity of formate ion. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The hydride complex [**1**][PF_6] was prepared as described[5]: ^1H NMR (DMSO-d_6 $\delta = -14.7$; IR (KBr pellet) ν_H 1827 cm^{-1}, ν_D 1292 cm^{-1}; UV−vis 500 nm ($8.5 \times 10^3\ M^{-1}\ cm^{-1}$); ESI MS in acetonitrile *m/z* 492.2 [Ru(terpy)(bpy)H$^+$ ^{102}Ru, relative intensity 100% in *m/z* range 200−1000]. The hydride complex undergoes very rapid exchange with the deuterons of D_2O, CD_3OD, and C_2D_5OD, probably via a dihydrogen complex, and reacts with acid ($k < 10^3\ M^{-1}\ s^{-1}$) to yield dihydrogen (yield ≥ 60%); the kinetics and mechanism of these reactions are currently under study. Manipulations were carried out under dim light. As noted by Konno et al.,[5] the hydride complex is not oxygen sensitive, but must be rigorously protected from the carbon dioxide in air. Thus reagents were prepared under argon with freshly drawn mill-Q water and transferred with use of syringe techniques. Kinetics runs were carried out with 0.03−0.1 mM RuH^+ and the C_1 species usually in at least 10-fold excess at 22 °C. Experiments with CO used 100% and 50% CO/50% Ar-saturated solutions in water (0.94 and 0.47 mM, respectively). Commercial CO_2/Ar mixtures were used to vary the [CO_2], and the reactions were monitored by diode array on an Applied Photophysics stopped-flow spectrometer. Mass spectra were simulated using Isotope Distribution Calculator (http://www2.sisweb.com/mstools/isotope.htm) and monitored on a Thermo Finnigan LCQ MS. Samples for comparison with the products of the C_1 reactions were synthesized as follows: CO_2 was reacted with RuH^+ in methanol to give the O-bonded formate complex as established by X-ray crystal structure by Konno et al.[5] The formaldehyde adduct was prepared through reaction of Ru(terpy)(bpy)(H_2O)$^{2+}$ with formaldehyde at pH 9 (borate buffer); this reaction is relatively rapid, evidently involving Ru−OH attack on CH_2O (substitution on carbon, not ruthenium). The methanol complex was prepared by dissolving Ru(terpy)(bpy)(H_2O)[PF_6]$_2$ in methanol for an hour, followed by evaporation to dryness. The digitized absorbance−time data from kinetics runs were least-squares-fit to an exponential function using Origin.
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