Coordination Chemistry Reviews, 64 (1985) 247—260
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

REDUCTION OF CARBON DIOXIDE BY TRIS(2,2'-BIPYRIDINE)COBALT(I)

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ABSTRACT

Preliminary stoichiometric and kinetic results bearing on the mechanism of the reduction of HCO_3^- to CO by tris(2,2'-bipyridine)cobalt(I) in aqueous media are reported. The results indicate that CO (not formate) is the dominant carbon product and that it is scavenged by $Co(bpy)_3^+$ to give insoluble $[Co(bpy)(CO)_2]_2$. At pH ~ 9, bicarbonate reduction occurs in competition with H_2O reduction. Both processes are inhibited by bpy and promoted by H^+, suggesting the common intermediate $Co(bpy)_2(H_2O)H^{2+}$. The bicarbonate reaction itself branches to give H_2 and CO in ~ 3:1 ratio.

INTRODUCTION

There has been considerable recent interest in the use of tris(2,2'-bipyridine)ruthenium(II) (2,2'-bipyridine = bpy) and its analogues as photosensitizers in photoconversion processes, primarily because of their spectral properties, the relative longevity of the MLCT excited states, and the facility of electron transfer processes involving both excited state and ground state species (refs. 2,3). A number of strategies have been developed for the reduction of water, based on either oxidative quenching of $^*Ru(bpy)_3^{2+}$ (with water reduction being performed by the reduced quencher), or reductive quenching (with water reduction involving either $Ru(bpy)_3^+$ or reducing species formed by reaction with it). In most cases, a heterogeneous catalyst (e.g. colloidal platinum) is required for hydrogen formation, but particularly significant exceptions are homogeneous systems using a cobalt(II) complex as catalyst. Scheme I involves reductive quenching by ascorbate ion (HAs^-) in the presence of added Co(II) (ref. 4).

I. Reductive Quenching

$Ru(bpy)_3^{2+} \xrightarrow{h\nu} {}^*Ru(bpy)_3^{2+}$
${}^*Ru(bpy)_3^{2+} + HAs^- \rightarrow Ru(bpy)_3^+ + HAs\cdot$
$HAs\cdot \rightarrow$ Products
$Ru(bpy)_3^+ + Co(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + Co(bpy)_3^+$
$Co(bpy)_3^+ + H_2O \rightarrow Co(bpy)_3^{2+} + 1/2\ H_2 + OH^-$

In Scheme II oxidative quenching by $Co(bpy)_3^{2+}$ in the presence of the electron

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donor triethanolamine (ref. 5; TEOA = triethanolamine, L = 4,7-$(CH_3)_2$phen, 50% aq. acetonitrile) yields H_2 with a quantum yield of 0.3.

II. Oxidative Quenching

$RuL_3^{2+} \xrightarrow{h\nu} {}^*RuL_3^{2+}$
${}^*RuL_3^{2+} + Co(bpy)_3^{2+} \longrightarrow RuL_3^{3+} + Co(bpy)_3^{+}$
$RuL_3^{3+} + TEOA \longrightarrow RuL_3^{2+} + TEOA\cdot^{+}$
$TEOA\cdot^{+} + TEOA \longrightarrow TEOA\cdot' + TEOAH^{+}$
$TEOA\cdot' + Co(bpy)_3^{2+} \longrightarrow Prod + Co(bpy)_3^{+}$
$Co(bpy)_3^{+} + H_2O \longrightarrow Co(bpy)_3^{2+} + 1/2\ H_2 + OH^-$

In either case the net photoinduced sequence is (Donor = TEOA or HAs^-):

$h\nu + Donor + Co(bpy)_3^{2+} \xrightarrow{[Ru(bpy)_3^{2+}]} Prod + Co(bpy)_3^{+}$
$Co(bpy)_3^{+} + H_2O \longrightarrow Co(bpy)_3^{2+} + OH^- + 1/2H_2$

The ability of cobalt complexes to promote homogeneous H_2 production appears unique, and the involvement of hydridocobalt species has been proposed.[4,5]

Lehn and Ziessel (ref. 6) have reported the photochemical reduction of carbon dioxide to carbon monoxide in 20% aq. acetonitrile using a system with constituents similar to II above. Reduction of ${}^*RuL_3^{2+}$ to RuL_3^{+} by triethanolamine or trialkylamines as quencher, followed by reduction of Co(II) to Co(I) (as $Co(bpy)_3^{+}$) by RuL_3^{+} was proposed. However, in light of recent results (ref. 5) characterizing H_2 formation in the triethanolamine, $Co(bpy)_3^{2+}$, Ru(4,7-$(CH_3)_2$phen$)_3^{2+}$ systems in aqueous acetonitrile the oxidative quenching sequence II also merits serious consideration for the CO_2 system. In related work, a 2,9-dimethyl-1,10-phenanthroline cobalt(II) complex also exhibits high CO_2-reduction activity in dimethylformamide (ref. 7).

Direct electrochemical reduction of CO_2 to produce CO, formate, or oxalate (ref. 8) is characterized by a large overpotential, and has been reported to occur at -2 V vs NHE. Chemically catalyzed electrochemical reductions on metal (ref. 9) and semiconducting (ref. 10) electrodes significantly lower the overpotential, and in some cases reduction (to CO plus CO_3^{2-}) occurs at -1.2 ± 0.1 V vs NHE in aqueous solution. Mediation of reduction of CO_2 to CO by photo- and electrogenerated $Re^0(bpy)(CO)_3Cl$ (ref. 7,11), and electrogenerated Ni^I(cyclam) (ref. 12) and (adsorbed) $Co^Ipc(H^-)$ (pc = phthalocyanine) (ref. 13) has also been found. Catalysis of the CO_2/HCO_2^- equilibrium by Pd(0) (ref. 14) and electroencapsulated Pd(0) has also been reported (ref. 15).

Activation of carbon dioxide to reduction by transition metal complexes has been attributed to insertion of CO_2 into metal-hydride bonds (producing formate) or disproportionation of CO_2 (producing CO and CO_3^{2-}) (ref. 16): in neither case is the intimate mechanism of the process known. In view of the intrinsic interest and importance of carbon dioxide activation and its light-promoted reduction, we have begun a study of the reactions of $Co(bpy)_3^+$ with water and bicarbonate ion in aqueous solution. Preliminary results are reported here.

EXPERIMENTAL SECTION

All manipulations were performed in a Vacuum Atmospheres glove box under an argon atmosphere, unless otherwise indicated. Solid $[Co(bpy)_3]Cl.H_2O$ was prepared as described previously (ref. 4) and recrystallized (ref. 17) by dissolving the crude solid (~ 300 mg) in dry ethanol (5 mL) containing 2,2'-bipyridine (770 mg). The solution was filtered, diethyl ether was added without stirring, and the Schlenk tube was stoppered and left undisturbed for 3 days. The blue/black crystals were collected, washed with ether and dried *in vacuo*. In some studies stock solutions of $Co(bpy)_3^+$ in ethanol were prepared by controlled potential electrolysis (E_{app} = -1.1 V vs aq SCE) of ~ 0.03 M $[Co(bpy)_3]Cl_2$ solutions using either carbon rod or platinum gauze working electrodes. Water used for all buffers was obtained from a MILLIPORE Milli-Q water purification system, and drawn immediately before deaeration with argon to avoid contamination by atmospheric CO_2. All materials were AR grade and were used without further purification.

Stoichiometry studies. In a typical run, 4.0 mL of the appropriate buffer (secondary amines react with CO_2 and so could not be used as buffers) containing $NaHCO_3$ and/or $Co(bpy)_3^{2+}$, if required, was transferred to a glass vessel (total volume = 13 mL) fitted with a serum cap. A 200 μL aliquot of a stock solution of $[Co(bpy)_3]Cl.H_2O$ in dry ethanol (containing bpy if required) was added by syringe, and the solution was stirred until completion of the reaction. H_2 and CO were determined by GC methods (molecular sieve 4A column thermostated at 150 °C, argon carrier gas, thermal conductivity detector); acidification of the solution was required prior to CO analysis.

The Co(I) concentrations in the stock solutions for the kinetic and stoichiometry studies were determined spectrophotometrically following reaction with either methyl viologen or $Os(bpy)_3^{3+}$.

Analysis for formate and oxalate ions present in product solutions from stoichiometric and kinetic studies was performed using a DIONEX 2010 Ion Chromatograph (HPICE-AS1 column; 10^{-3} M HCl/2% acetonitrile eluent). The reactions were run in TRIS-HCl media because borate and sulfate interfered with the formate determinations.

Kinetic studies. In a typical run, a 200 μL aliquot of a stock solution of $[Co(bpy)_3]Cl.H_2O$ in dry ethanol (containing bpy if required) was added to 4.0 mL of the appropriate buffer (containing $NaHCO_3$ and/or $Co(bpy)_3^{2+}$ if required) in a 1 cm cell. The cell was immediately stoppered, removed from the glovebox, and the decay of Co(I) measured spectrophotometrically (605 nm) for 3-4 half-lives. The infinity reading was obtained after exposing the solution to air, and the pH was measured.

Formation and analysis of $[Co(bpy)(CO)_2]_2$

Reaction of $Co(bpy)_3^+$ with HCO_3^-. A solution of $[Co(bpy)_3]Cl{\cdot}H_2O$ (70 mg) in ethanol (1.5 mL) was added to 17.5 mL of 0.20 M boric acid buffer (pH 9.2; $[Co(bpy)_3^+]$ = 7.8 mM; $[Co(bpy)_3^{2+}]$ = 2.5 mM; μ = 0.5 M, Na_2SO_4) containing 100 mg $NaHCO_3$ (0.063 M). The blue solution was stirred until completion of the reaction was indicated by the pale yellow solution and dark precipitate. After ~ 1 hour the black precipitate was filtered under argon, washed with water and dried *in vacuo*. The yield was low and somewhat variable.

Reaction of $Co(bpy)_3^+$ with CO. A solution of $[Co(bpy)_3]Cl{\cdot}H_2O$ (90 mg) in dry ethanol (12 mL) was stirred under a CO atmosphere for 15 minutes. The black product was filtered under argon, washed with ethanol, and dried *in vacuo*. Yield 20 mg, 95%.

Analysis. CO was determined by acidification of a weighed sample in a closed vessel followed by GC analysis of the gas above the solution. Cobalt was determined by atomic absorption spectroscopy and x-ray fluorescence, and bpy spectrophotometrically.

RESULTS AND DISCUSSION

General Considerations

In neutral aqueous solution the overall thermodynamic requirements for reduction of water to hydrogen and of carbon dioxide to CO or formate are similar:

TWO-ELECTRON REDUCTION, pH 7, 25 °C (ref. 18), vs NHE

$$2H_2O_{(\ell)} + 2e \rightarrow H_{2(g)} + 2OH^-_{(aq)} \qquad E^o = -0.41\ V$$

$$CO_{2(g)} + H_2O_{(\ell)} + 2e \rightarrow CO_{(g)} + 2OH^-_{(aq)} \qquad E^o = -0.53\ V$$

$$CO_{2(g)} + H_2O_{(\ell)} + 2e = HCO_{2(aq)}^- + OH^-_{(aq)} \qquad E^o = -0.31\ V$$

Moreover, in seeking catalysts for these reactions similar issues arise. Both reductions are very difficult via one-electron processes, since the one-electron reduction products H atom and $\cdot CO_2^-$ (formate radical) are extremely energetic species. By using pulse-radiolytic methods, Schwarz and Dodson have recently determined E° for the $CO_2/\cdot CO_2^-$ couple to be -1.9 V vs NHE in water (ref. 19), and the intrinsic barrier for this one-electron reduction is estimated to be ca. 0.6 V (ref. 20). The $\cdot CO_2^-/:CO_2^{2-}$ potential has been estimated to be -1.2 V vs. NHE (ref. 21). Values for $H^+/H\cdot/H^-$ have been discussed previously (ref. 2).

ONE-ELECTRON REDUCTION, pH 7, 25 °C, vs NHE

$$H^+ \xrightarrow{-2.7\ V} H\cdot \xrightarrow{+0.03\ V} H^-$$

$$CO_2 \xrightarrow{-1.9\ V} \cdot CO_2^- \xrightarrow{-1.2\ V} :CO_2^{2-}$$

Thus in either H_2O or CO_2 reduction, paths involving the (free) one-electron reduction products are expected to be vanishingly slow and means of circumventing these paths or stabilizing the one-electron species are sought. In the H_2O/H_2 reaction, metal hydride complexes may provide catalytic routes. In the CO_2/CO or HCO_2^- reaction, catalysis by metal complexes may involve coordination of carbon dioxide (ref. 22) or insertion into a metal hydride bond to yield a formate species (ref. 23).

As will be seen, comparison of the above parameters for H_2O and CO_2 reduction is particularly appropriate in the present system because, in the presence of HCO_3^-, these reactions occur in competition with each other and even appear to involve a common intermediate. Interestingly, the presence of water is required in a number of systems when CO_2 reduction occurs. Unfortunately, the presence of water also complicates the issue of the carbon substrate undergoing reduction. In aqueous media the following equilibria must be considered:

$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$ $\quad K = 3 \times 10^{-2}\ M\ atm^{-1}$

$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3$ $\quad K = 2.6 \times 10^{-3}$

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $\quad K = 2.5 \times 10^{-5}\ M$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ $\quad K = 1.6 \times 10^{-10}\ M$

(The equilibrium constants given are appropriate to ~ 0.5 M ionic strength, 25 °C (ref. 24).) Above pH 10 and below pH 4, "CO_2" solutions contain CO_3^{2-} and H_2CO_3/CO_2, respectively. Near pH 7, the three species HCO_3^-, CO_2 and H_2CO_3 are all present and their distribution is pH dependent. Consequently pH variations carried out to assess the role of H^+ in CO_2 reduction systems may be difficult to interpret when the dominant "CO_2" form(s) change.

Furthermore, the equilibration of gaseous and aqueous CO_2 must be taken into account: Depending upon the experimental procedures (and time scales) the above equilibria may lead to substantial changes in the CO_2 partial pressure above a solution and in the concentration(s) of dissolved species.

Finally, the free-energy change for "CO_2" reduction is a function of the substrate and pH. Fig. 1 summarizes these data in graphic form.

pH	Half-Reaction	E^0, V	H^+/H_2 E^0,V
0	$CO_{2(g)} + 2H^+ + 2e = CO_{(g)} + H_2O$	-0.12	-0.00
7	$HCO_3^- + 3H^+ + 2e = CO_{(g)} + 2H_2O$	-0.48	-0.41
9	$HCO_3^- + 3H^+ + 2e = CO_{(g)} + 2H_2O$	-0.66	-0.53
11	$CO_3^{2-} + 4H^+ + 2e = CO_{(g)} + 2H_2O$	-0.87	-0.65

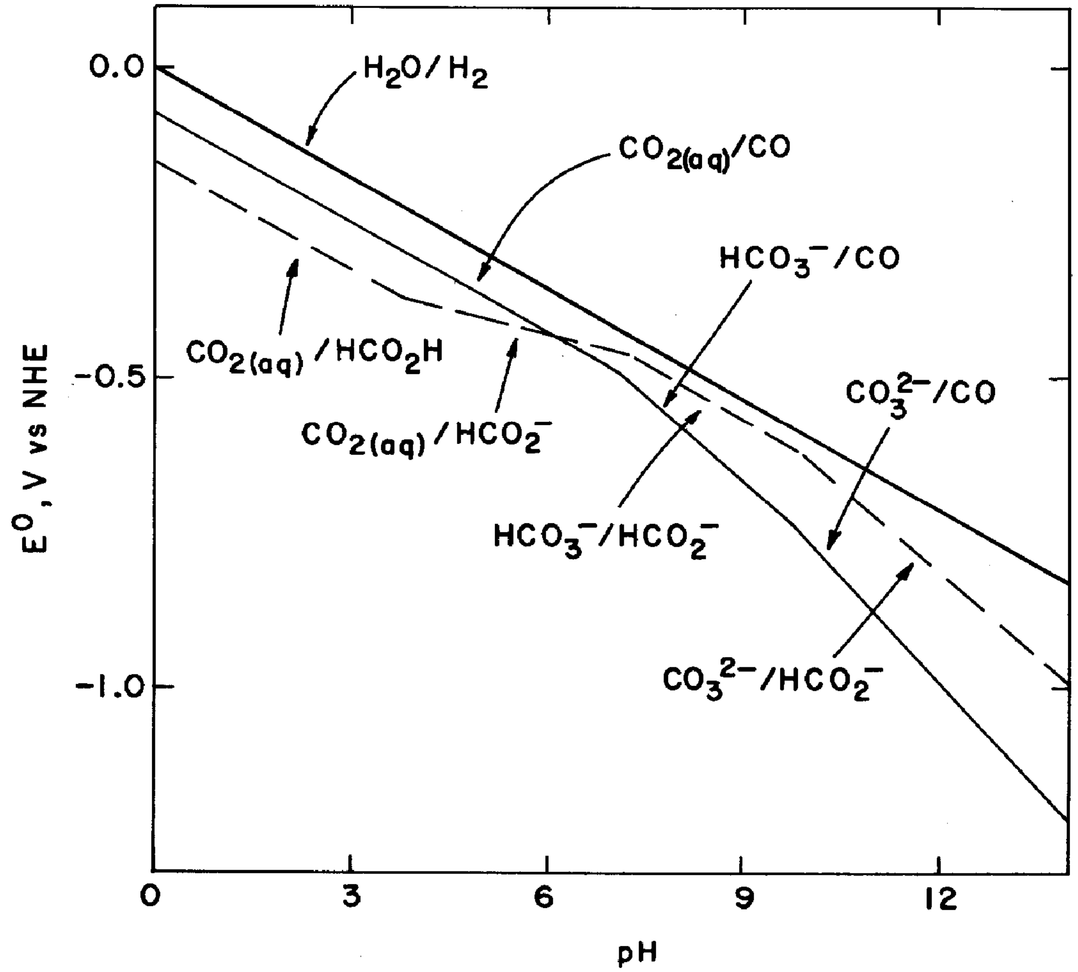


Fig. 1. E^0 values (vs NHE) for two-electron reduction of H_2O and CO_2 as a function of pH and the dominant forms of reactants and products. The following standard state conventions are used: H_2O, liquid; H_2 and CO, gas (i.e., 1 atm); CO_2, HCO_2H, HCO_2^-, HCO_3^-, and CO_3^{2-}, aqueous (i.e., 1 M).

General Features of the $Co(bpy)_3^+/H_2O/HCO_3^-$ System

No reaction of $Co(bpy)_3^+$ with CO_2 is found in dry ethanol over several days. However, reaction does occur in aqueous media. This system (like others, refs. 6,9,10) is complicated by side-reactions: $Co(bpy)_3^+$ also reacts with water to yield H_2 at pH > 7 and dihydrobipyridines at lower pH (ref. 4). These products reflect the fact that $Co(bpy)_3^+$ is a strong reductant: $E^o(Co(bpy)_3^{2+/+}) = -0.95$ V and $E^o(Co(bpy)_3^{3+/+}) = -0.33$ V (ref. 5). Accordingly, in aqueous media CO_2 reduction must occur in competition with these reactions. As noted above, an additional complication is the pH-dependent $CO_3^{2-}/HCO_3^-/CO_2$ equilibria. In the pH-range considered here HCO_3^- is the dominant form with CO_3^{2-} = 1-10% and $CO_{2(aq)}$ < 3% of the total "CO_2" species and is therefore considered the reactant.

The reaction was studied spectrophotometrically by observing the disappearance of $Co(bpy)_3^+$ in aqueous buffer solutions under anaerobic conditions in the presence and absence of HCO_3^-. The competition of H_2O and HCO_3^- for $Co(bpy)_3^+$ is illustrated in Fig. 2. While it is evident that the rate of $Co(bpy)_3^+$ consumption increases linearly with $[HCO_3^-]$, it is also evident that there is a relatively large intercept. The latter is due to the reaction with water, which gives H_2 according to eq. 1 (ref. 4) in > 70% yield.

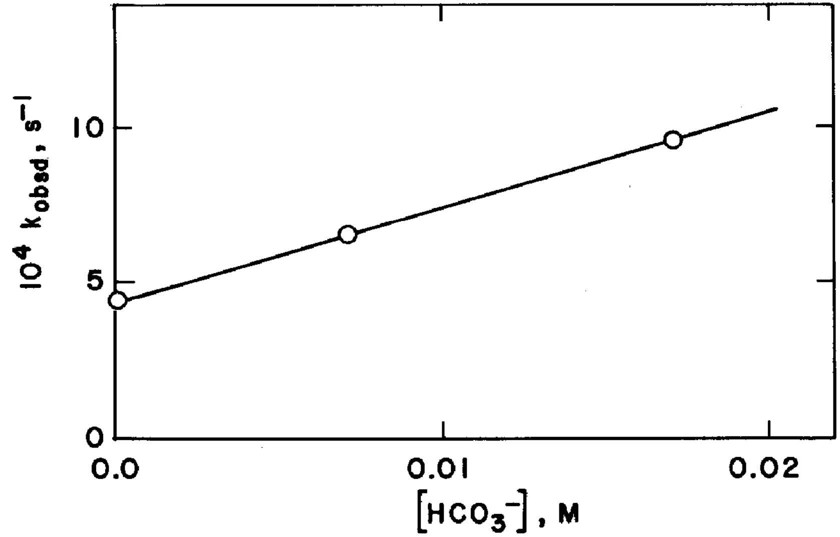


Fig. 2. Pseudo-first-order rate constants (25 °C) for the disappearance of $Co(bpy)_3^+$ in borate buffer (pH 8.8) as a function of $[HCO_3^-]$ (0.16 mM Co(I); 2.4 mM $Co(bpy)_3^{2+}$; 4.8% ethanol; ionic strength = 0.5 M, Na_2SO_4).

$$Co(bpy)_3^+ + H_2O \longrightarrow Co(bpy)_3^{2+} + 1/2\ H_2 + OH^- \qquad (1)$$

Not only does HCO_3^- accelerate the rate of consumption of $Co(bpy)_3^+$, but it also reduces the amount of H_2 formed. This is illustrated in Fig. 3 where H_2 yields are plotted as a function of $[HCO_3^-]$ for TRIS buffers at pH 8.4.

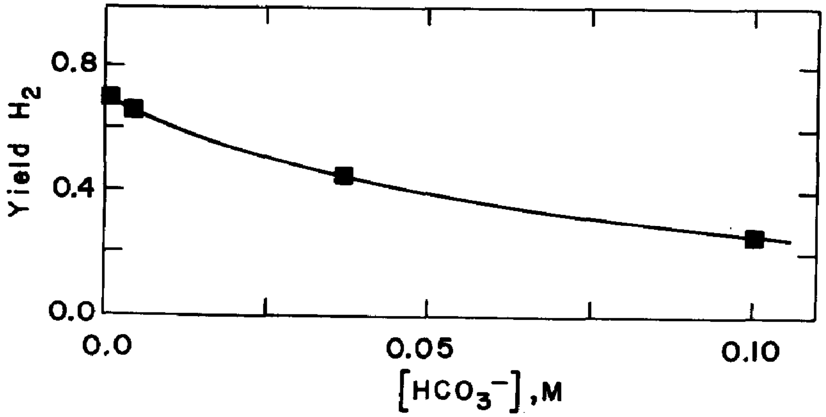
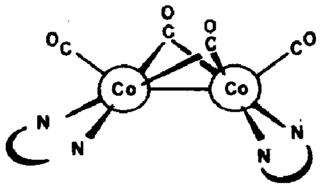


Fig. 3. Hydrogen yields (based on eq. 1) as a function of $[HCO_3^-]$ in TRIS buffer at pH 8.4 (1.4 mM Co(I); 4.8% ethanol; ionic strength = 0.5 M, Na_2SO_4).

CO_2/HCO_3^- Reduction Product

On G.C. analysis of the gas above the reaction solutions with HCO_3^- present (pH 8.4-9.5), no free CO was detected, and although formate ion was found by ion chromatographic analysis of the solution, it was not formed in significant amounts (< 1%). In the stoichiometry studies at high $[HCO_3^-]$ with high [Co(I)], small amounts of a dark solid were formed. This product showed IR absorptions at 1933, 1895 and 1717 cm^{-1}: the product obtained from similar experiments using $H^{13}CO_3^-$ gave equivalent absorptions at 1891, 1852 and 1679 cm^{-1}, respectively, indicating that the absorptions arise from carbonyl groups formed during the reduction process. A product with identical IR spectral properties and analytical data (Co/bpy = 1:1, Co/CO ~ 1:2) is produced by the reaction of $Co(bpy)_3^+$ with CO in ethanol. It seems clear that the product of both reactions is the same as the product formed by reduction of Co(II) by BH_4^- in the presence of bpy and CO (ref. 25), or by the reaction of $(norbornadiene)_2Co_2(CO)_4$ with bpy (ref. 26). The structure of this complex has been assigned as $[Co(bpy)(CO)_2]_2$ (C_{2v}) (as distinct from the geometric



isomer (C_{2h}) with the terminal CO groups trans) on the basis of group theory analysis of the IR spectrum. The complex is stable in contact with basic solution, but, upon acidification to pH < 1, decomposes to liberate ~ 2 mols CO per Co and ~ 1 mol H_2 per Co (eq. 2), consistent with the above formulation.

$$[Co(bpy)(CO)_2]_2 + 6H^+ \rightarrow 4CO + 2H_2 + 2Co^{2+}_{aq} + 2bpyH^+ \qquad (2)$$

Thus these results indicate that CO (rather than formate) is the major product of HCO_3^- reduction by $Co(bpy)_3^+$ (eq. 3, where the CO may be free or bound to cobalt). The CO produced is scavenged by $Co(bpy)_3^+$ to give

$$2Co(bpy)_3^+ + HCO_3^- + H_2O \rightarrow 2Co(bpy)_3^{2+} + CO + 3OH^- \qquad (3)$$

$$Co(bpy)_3^+ + CO \rightarrow 1/4[Co(bpy)(CO)_2]_2 + bpy + 1/2\ Co(bpy)_3^{2+} \qquad (4)$$

insoluble $[Co(bpy)(CO)_2]_2$ (eq. 4). Subsequent acidification of the product solution decomposes the cobalt carbonyl dimer (eq. 2) allowing determination of CO as the gas.

In Fig. 4, H_2 and CO yields are compared. The H_2 yields (based on

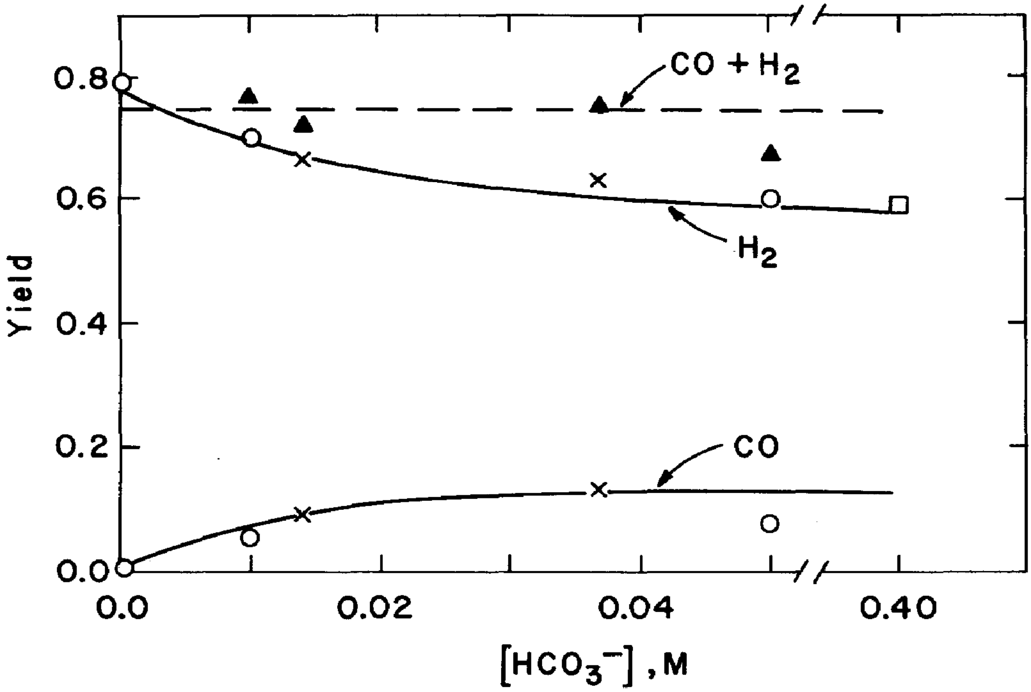
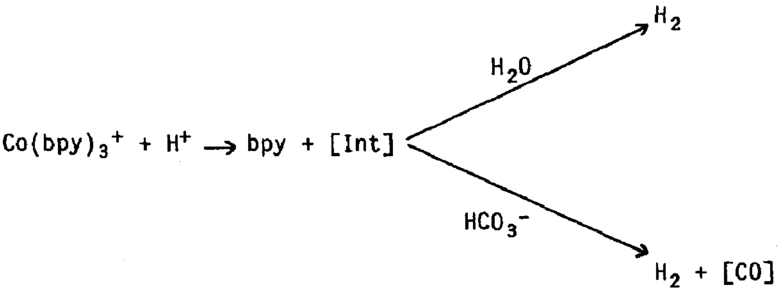


Fig. 4. Balance of yields of CO/H_2 from reaction of $Co(bpy)_3^+$ with HCO_3^- in aqueous solution: x,$[Co(I)]_0 = 0.66$ mM; 0.2 M boric acid buffer, pH 8.8; $\mu = 0.5$ M, Na_2SO_4; no Co(II). ○$[Co(I)]_0 = 0.74$ mM, $[Co(II)]_0 = 0.74$ mM; 0.4 M boric acid buffer, pH 8.8, $\mu = 0.5$ M, Na_2SO_4. □$[Co(I)]_0 = [Co(II)]_0 = 0.74$ mM, 0.4 M $NaHCO_3$, pH 8.8, $\mu = 0.5$ M. No excess bpy, 4.8% ethanol. H_2 yield = 2 x (mols H_2 per mol Co(I) taken) (where H_2 is determined prior to acid addition) and CO yield = 3 x (mols CO per mol Co(I) taken). ▲ Sum of H_2 and CO yields.

eq. 1) were determined prior to acid addition so that H_2 from eq. 2 is not included. The CO yields are calculated on the basis of eq. 3 and eq. 4, i.e., $3Co(bpy)_3{}^+$ are consumed per CO detected. With the yields so defined the sum of the yields should be constant if no other products are formed. From Fig. 3 it is evident that reasonable constancy is found.

Kinetics and Product Yields

The kinetics studies were focussed primarily on the behavior of the system in the absence and presence of low added bpy in the pH range 8.4-9.5. Within the pH range studied, there is a minor contribution to the rate from a parallel pathway whose rate expression shows a square dependence on [Co(I)] and $[H^+]$ and an inverse dependence on $[Co(bpy)_3{}^{2+}]$ (ref. 27). The Co(II) salt was therefore added to many of the kinetic and stoichiometric runs to suppress this contribution. Some kinetic details of the pathway are known, and its involvement in the $HCO_3{}^-$ reduction processes under the conditions used appears negligible. Under the present conditions the rate is first-order in $[Co(bpy)_3{}^+]$, first order in $[H^+]$, and first order in $[HCO_3{}^-]$. The rate of eq. 1 (i.e. no added $HCO_3{}^-$) is first order in both $[Co(bpy)_3{}^+]$ and $[H^+]$ (ref. 27). The rates of both reactions are inhibited by bpy, indicating loss of bpy prior to the rate-determining step. The observations suggest that $HCO_3{}^-$ and H_2O (eq. 1) may compete for a common intermediate formed from $Co(bpy)_3{}^+$ and H^+ with loss of bpy -- possibly $Co(bpy)_2(H_2O)H^{2+}$ (ref. 28). [The analogous rhodium complex has also been characterized (ref. 29).] Previous studies (ref. 4) of the stoichiometry of the $Co(bpy)_3{}^+/H_2O$ reaction have also demonstrated inhibition of the H_2-yield by excess bpy. Stoichiometry studies show that the $Co(bpy)_3{}^+/HCO_3{}^-$ reaction is also suppressed by the presence of excess bpy, so that as the bpy concentration increases, $HCO_3{}^-$ eventually does not affect the H_2-yield for the water reduction reaction. These observations also support the competition of H_2O and $HCO_3{}^-$ for the same intermediate, e.g.,



where [CO] denotes the $HCO_3{}^-/CO_2$ reduction product $[Co(bpy)(CO)_2]_2$.

Note, however, that in the pH range studied a rate law such as $-d[Co(bpy)_3^+]/dt = a[Co(bpy)_3^+][H^+][HCO_3^-]/[bpy]$ is kinetically indistinguishable from $-d[Co(bpy)_3^+]/dt = a'[Co(bpy)_3^+][CO_2]/[bpy]$. The first expression suggests rate-determining reaction of $Co(bpy)_2(H_2O)H^{2+}$ with HCO_3^- while the second suggests reaction of $Co(bpy)_2^+$ (ref. 20) with CO_2 (generated through the pre-equilibrium $H^+ + HCO_3^- = CO_2 + H_2O$) to give a CO_2 complex. Thus our data do not rule out reaction pathways such as the latter. In fact it is even possible that the two occur in parallel.

Finally, in addition to the parallel reactions with water and bicarbonate ion discussed above, there is also evidence that the HCO_3^- reaction itself gives both H_2 and CO. In Fig. 5 the ratio of HCO_3^- to H_2O paths as evaluated from the kinetics is plotted as a function of $[HCO_3^-]$. Also shown (solid symbols) are CO-to-H_2 ratios obtained from product analysis of comparable solutions. While the CO-to-H_2 ratio rises between 0 and ~ 0.03 M HCO_3^-, it levels off at higher $[HCO_3^-]$ attaining a limiting value of ~ 0.3 at pH 9 under the conditions shown. Preliminary evidence indicates this

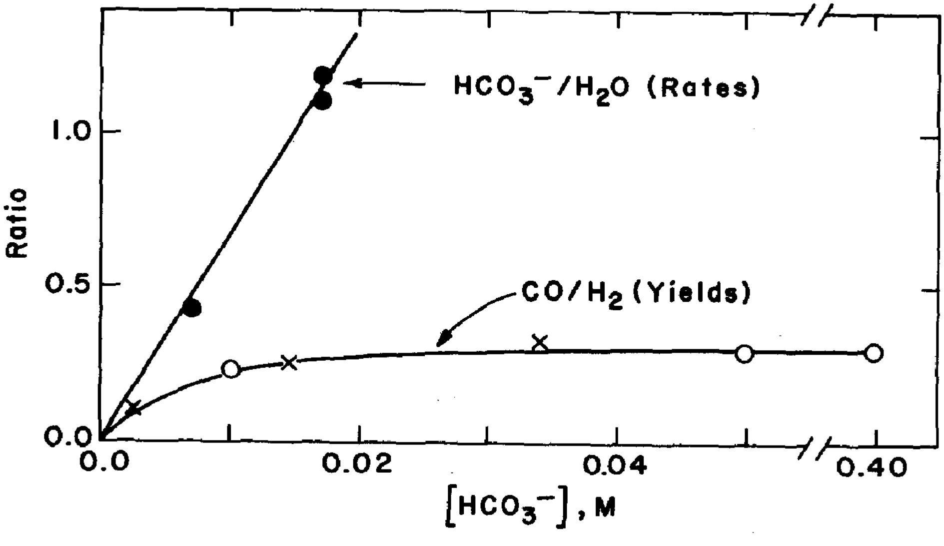


Fig. 5. $Co(bpy)_3^+/HCO_3^-$ reaction in borate buffers, pH 8.4-9.5 (no added bpy; 4.8% ethanol; ionic strength = 0.5 M, Na_2SO_4). The solid symbols are associated with kinetic measurements (see Fig. 2) and the other symbols with product measurements (see Fig. 4). The ratios are defined by (stoichiometric) $R_{HCO_3^-}/R_{H_2O} = 3(a_{H_2O} - a_{HCO_3^-})/2a_{H_2O}$ where a_{H_2O} = mols H_2 per Co(I) formed in the absence of HCO_3^- and $a_{HCO_3^-}$ = mols H_2 per Co(I) with added bicarbonate, and (kinetic) $R_{HCO_3^-}/R_{H_2O} = (k_{obsd,HCO_3^-} - k_{obsd,H_2O})/k_{obsd,H_2O}$ where k_{obsd,HCO_3^-} and k_{obsd,H_2O} are the pseudo-first-order rate constants for $Co(bpy)_3^+$ reaction in the presence and absence of bicarbonate.

partitioning to be variable: for example, the ratio is higher in TRIS (Fig. 2) than in borate buffer and much lower in pH 7 phosphate buffer. Analogous changes in branching ratio have been reported by Lehn and Ziessel who noted the sensitivity of this ratio to substituents on the tertiary amines; CO production was found to be favored in the order $N(C_2H_5OH)_3 > N(n\text{-propyl})_3 > N(Et)_3 > N(CH_3)_3$ (ref. 6). The fact that the HCO_3^- reaction branches may reflect the fact that (bound) HCO_3^- may act as either a proton source (to give H_2) or a "carbon" source (to give CO), but the origin of the sensitivity of the branching ratio to the nature of the buffer is not obvious. In any case it is noteworthy that the thermodynamic ratio of H_2 to (free) CO is ~ 10^2 at pH 9. The fact that relatively high yields of CO are observed in the present $Co(bpy)_3^+$ system may be due to the $Co(bpy)_3^+$ scavenging of CO (eq. 4) which drives the reaction. Alternatively, the observed partitioning may solely reflect kinetic (as opposed to thermodynamic) factors.

Formate ion is a minor product in the $Co(bpy)_3^+ - HCO_3^-$ reaction (CO: HCO_2^- ~ 10:1). Interestingly, the reduction of HCO_3^- or CO_2 to HCO_2^- is favored on thermodynamic grounds over (gaseous) CO formation above pH ~ 6 (see Fig. 1). The fact that the CO produced in the $Co(bpy)_3^+$ reaction is not free but converted to $[Co(bpy)(CO)_2]_2$ does, of course, cloud the picture somewhat; possibly the formation of the insoluble dimer does help to drive CO formation thermodynamically. In any event, we have shown that "CO" is a primary product; added formate is not converted to "CO" under the reaction conditions. Thus the fact that HCO_2^- is produced in such small yield (relative to CO) suggests kinetic control of the product distribution. Formate ion is the expected product for reaction of (molecular) CO_2 with a metal hydride (insertion into the M-H bond). In the $Co(bpy)_3^+$ system, such a pathway would be manifested as $-d[Co(bpy)_3^+]/dt = b[Co(bpy)_3^+][H^+]^2[HCO_3^-]/[bpy]$ at pH > 7. Although our kinetic data (pH $\geq$ 8.5) do not indicate an $[H^+]^2$-dependence, a small ($\leq$ 10%) contribution from this term cannot be ruled out. Thus the formate may arise from such a reaction. However, as discussed above, from the observed kinetics and product distribution, the major "bicarbonate" reaction involves either HCO_3^- attack on $Co(bpy)_2(H_2O)H^{2+}$ or CO_2 attack on $Co(bpy)_2(H_2O)_2^+$ (or both).

SUMMARY

In aqueous bicarbonate solutions (pH 8.5 - 10) $Co(bpy)_3^+$ reacts with water to give H_2 and with HCO_3^- to give H_2, CO (as the insoluble $[Co(bpy)(CO)_2]_2$), and some HCO_2^-, with the extent of reaction with HCO_3^- increasing as $[HCO_3^-]$ increases. The rate laws for reaction with H_2O and HCO_3^- are first-order in $[Co(bpy)_3^+]$ and $[H^+]$ and inverse in [bpy]. Thus both water and HCO_3^- reactions may involve the hydride $Co(bpy)_2(H_2O)H^{2+}$ as intermediate. (Of course, kinetically equivalent pathways -- such as, for HCO_3^-, reaction of $Co(bpy)_2(H_2O)_2^+$ with CO_2 -- cannot be ruled out.) In the HCO_3^--reaction the branching between H_2 and CO depends upon the nature of the buffer and favors H_2 over CO in about a 3-to-1 ratio in borate media.

ACKNOWLEDGMENTS

This research was carried out at Brookhaven National Laboratory which is operated under contract DE-AC-02-76-CH00016 with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences. FRK acknowledges financial assistance of the Australian-American Educational Foundation through a Fulbright Award. We thank Ms. E. Norton for performing the Co, Cl, and bpy analyses.

REFERENCES

1 On an approved Special Studies Program from the Department of Chemistry and Biochemistry, James Cook University of North Queensland, Townsville, Queensland 4811, Australia.

2 N. Sutin and C. Creutz, Pure and Appl. Chem., 52 (1980) 2717-2738; and references cited therein.

3 K. Kalyanasundaram, Coord. Chem. Rev., 46 (1982) 159-244; and references cited therein.

4 C.V. Krishnan, C. Creutz, D. Mahajan, H.A. Schwarz and N. Sutin, Israel J. Chem., 22 (1982) 98-106.

5 C.V. Krishnan, C. Creutz, B.S. Brunschwig and N. Sutin, J. Am Chem. Soc., in press.

6 J.-M. Lehn and R. Ziessel, Proc. Nat. Acad. Sci. USA, 79 (1982) 701-704.

7 J. Hawecker, J.-M. Lehn and R. Ziessel, J. Chem. Soc., Chem. Commun., (1983) 536-538.

8 C. Amatore and J.-M. Saveant, J. Am. Chem. Soc., 103 (1981) 5021-5023.

9 B. Fisher and R. Eisenberg, J. Am. Chem. Soc., 102 (1980) 7361-7363.

10 (a) M.G. Bradley, T. Tysak, D.J. Graves and N.A. Vlachopoulos, J. Chem. Soc., Chem. Commun., (1983) 349-350. (b) K.W. Freese, Jr. and D. Canfield, J. Electrochem. Soc., 131 (1984) 2518.

11 H. Hawecker, J.M. Lehn, and R. Ziessel, J. Chem. Soc., Chem. Commun., (1984) 328-330.

12 M. Beley, J.P. Collins, R. Rupert, and J.-P. Sauvage, J. Chem. Soc., Chem. Commun., (1984) 1315-1316.

13 C.M. Lieber and N.S. Lewis, J. Am. Chem. Soc., 106 (1984) 5033-5034.

14 C.J. Stalder, S. Chao, D.P. Summers, and M.S. Wrighton, J. Am. Chem. Soc., 105 (1983) 6318-6320.

15 C.J. Stalder, S. Chao, and M.S. Wrighton, J. Am. Chem. Soc., 106 (1984) 3673-3675.

16 S. Inune and N. Yamazaki (Eds.), Organic and Bioorganic Chemistry of Carbon Dioxide, Kodansha Ltd., Tokyo, Wiley, New York, 1982.

17 D.J. Szalda, C. Creutz, D. Mahajan and N. Sutin, Inorg. Chem., 22 (1983) 2372-2379.

18 W. M. Latimer, Oxidation Potentials, Prentice-Hall, Englewood Cliffs, NJ (1952).

19 H.A. Schwarz and R.W. Dodson, to be submitted for publication.

20 H.A. Schwarz, C. Creutz and N. Sutin, Inorg. Chem., 24 (1985) xxxx.

21 J. Lilie, G. Beck and A. Henglein, Ber. Bunsenges, Phys. Chem., 75 (1971) 458-465.

22 (a) S. Gambarotta, F. Arena, C. Floriani and P.F. Zanazzi, J. Am. Chem. Soc., 104 (1982) 5082-5092. (b) R. Eisenberg and D.E. Hendrickson, Adv. Catalysis, 28 (1979) 79-172.

23 (a) A. Yamamoto, S. Kitazume, L.S. Pu and S. Ikeda, J. Am. Chem. Soc., 93 (1971) 371-380. (b) A. Misono, Y. Uchida, M. Hidai and T. Kuse, Chem. Commun., (1968) 981. (c) B.P. Sullivan and T.J. Meyer, J. Chem. Soc., Chem. Commun., (1984) 1244-1245. (d) S. Slater and J.H. Wagenknecht, J. Am. Chem. Soc., 106 (1984) 5367-5368.

24 D. A. Palmer and R. van Eldik, Chem. Rev., 83 (1983) 651-731.

25 G. Mestroni, A. Camus and E. Mestroni, J. Organomet. Chem., 24 (1970) 775-781.

26 H. Behrens and W. Aquila, Z. Anorg. Allg. Chem., 356 (1967) 8-21.

27 F.R. Keene, D. Mahajan, S.F. Chan, C. Creutz and N. Sutin, work in progress.

28 C. Creutz, H.A. Schwarz and N. Sutin, J. Am. Chem. Soc., 106 (1984) 3036.

29 M. Chou, C. Creutz, D. Mahajan, N. Sutin and A.P. Zipp, Inorg. Chem., 21 (1982) 3989-3997.