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NOTE

Hydricity of transition-metal hydrides and its role in CO_2 reduction[†]

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The role of C—H bond formation in the reduction of carbon dioxide, mediated by metal and palladium phosphine catalysts is studied. Copyright © 2000 John Wiley & Sons, Ltd.

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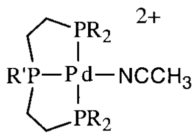
INTRODUCTION

The electrochemical reduction of CO_2 to fuels such as methanol or methane requires the cleavage of at least one C—O bond and the formation of three or four C—H bonds. Research efforts in our laboratory are focused on an increased understanding of these two primary steps in the electrocatalytic reduction of CO_2. Previous research in our laboratory has shown that palladium complexes **1** and **2** are catalysts for the electrochemical reduction of CO_2 to CO in acidic organic solvents.[1]



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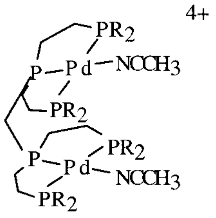

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This reaction involves the cleavage of a C—O bond. Extensive kinetic studies of complexes with designed structural modifications indicate that this bond cleavage involves a deinsertion reaction in which either a hydroxide or water molecule is transferred to palladium. This reaction requires a vacant coordination site so that the hydroxide ion or water molecule can migrate from carbon to the metal. This site is created by the loss of the weakly coordinated acetonitrile shown for structures **1** and **2**. This vacant coordination site appears to be necessary for electrocatalysts to achieve high catalytic rates at low overpotentials.

C—H bond formation is also an important step in the electrocatalytic reduction of CO_2. However, our understanding of the thermodynamics and kinetics of C—H bond-forming processes in electrocatalytic reactions are extremely limited. The objective of the research described in this paper is to provide insight into the thermodynamics of this fundamental reaction.

RESULTS AND DISCUSSION

We have shown previously that $[HM(diphosphine)_2]^+$ complexes can be generated by electrochemical reduction of $[M(diphosphine)_2]^{2+}$ cations in protic solvents and that these hydrides are capable of reducing coordinated CO to produce formyl complexes, reactions [1] and [2] (L = diphosphine ligand).[2] These are two potentially important steps in the electrocatalytic reduction of CO, the product of CO_2 reduction with the catalysts described above.

$$[M(L)_2]^{2+} + 2e^- \longrightarrow M(L)_2 \xrightarrow{H^+} [HM(L)_2]^+ \qquad [1]$$

$$[HM(L)_2]^+ + [M'L'_n(CO)]^+ \rightarrow [M(L)_2]^{2+} + [M'L'_n(CHO)] \qquad [2]$$

Whether reaction [2] occurs or not depends on the hydride donor ability of the $[HM(L)_2]^+$ complexes (i.e. their thermodynamic hydricity) and the

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hydride acceptor ability of the carbonyl complexes. In this paper we examine those features that determine the thermodynamic hydricity of $[\mathrm{HM(diphosphine)_2}]^+$ complexes (where M = Pt or Ni). The thermodynamic cycle shown in reactions [3]–[6] was used to measure this property. This cycle is similar to the method used by Tilset and co-workers[3] for obtaining thermodynamic data for M—H bond energies for transition metal hydrides. It requires a knowledge of the $\mathrm{p}K_{\mathrm{H}^+}$ values for the hydride complexes under study and the redox potentials for two sequential oxidations of the $\mathrm{M(diphosphine)_2}$ complexes formed upon deprotonation of the $[\mathrm{HM(diphosphine)_2}]^+$ cations.

$$\mathrm{L_2MH^+} \rightarrow \mathrm{L_2M} + \mathrm{H^+} \qquad \Delta G^{\circ} = 1.37\,\mathrm{p}K_{\mathrm{H}^+} \qquad [3]$$

$$\mathrm{L_2M} \rightarrow \mathrm{L_2M^{2+}} + 2\mathrm{e^-} \qquad \Delta G^{\circ} = 46.1\,E^{\circ}(+2/0) \qquad [4]$$

$$\underline{\mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{H^-}} \qquad \underline{\Delta G^{\circ} = 79.6} \qquad [5]$$

$$\mathrm{L_2MH^+} \rightarrow \mathrm{L_2M^{2+}} + \mathrm{H^-} \qquad \Delta G^{\circ}_{\mathrm{H}^-} = 1.37\,\mathrm{p}K_{\mathrm{H}^+} + 46.1\,E^{\circ}(\mathrm{II}/0) + 79.6 \qquad [6]$$

Table 1 Thermodynamics of hydride ($\Delta G^{\circ}_{\mathrm{H}^-}$)transfer reactions for $[\mathrm{HM(diphosphine)_2}]^+$ and CpM(CO)(L)H complexes in acetonitrile

M	L	$\mathrm{p}K_{\mathrm{H}^+}$	$E_{1/2}$(II/0) (V)	$\Delta G^{\circ}_{\mathrm{H}}$ (kcal $\mathrm{mol^{-1}}$)
Ni[a]	dppe	14.2	−0.79	62.7
	dmpp	23.9	−1.11	61.2
	depe	23.8	−1.22	56.0
Pt[a]	dppe	22.0	−1.24	52.5
Ni[a]	dmpe	24.3	−1.39	48.9
Pt[a]	dmpp	27.8	−1.53	47.2
	depe	27.1	−1.65	40.8
	dmpe	28.5	−1.73	38.8
CpMo[b]	CO			88.6
$\mathrm{Cp(CO_2Me)W}$[b]	CO			85.0
Cp*Mo[b]	CO			84.7
CpW[b]	CO			83.2
CpMo[b]	$\mathrm{PPh_3}$			81.7
Cp*W[b]	CO			81.4
CpMo[b]	$\mathrm{PMe_3}$			79.4

[a] Data taken from Ref. 5.
[b] Data taken from Ref. 6.

The $\mathrm{p}K_{\mathrm{H}^+}$ values were determined by studying equilibrium reactions (in acetonitrile and benzonitrile) between the metal hydrides and bases whose $\mathrm{p}K_{\mathrm{H}^+}$ values are known.[4] The redox potentials were measured by cyclic voltammetry.

The relative hydricities ($\Delta G^{\circ}_{\mathrm{H}^-}$values) of a series of $[\mathrm{HM(diphosphine)_2}]^+$ complexes are shown in Table 1 [where M = Ni and Pt; and diphosphine = bis(dimethylphosphino)ethane (dmpe), bis(diethylphosphino)ethane (depe), bis(diphenylphosphino) ethane (dppe), and bis(dimethylphosphino)propane (dmpp)].[5] The $\mathrm{p}K_{\mathrm{H}^+}$ values for the hydride complexes and the $E_{1/2}$ values (versus ferrocene) for the average of the Ni(I/O) and Ni(II/I) couples or the Pt(II/0) couples are also shown in Table 1. It can be seen from Table 1 that the order of $\Delta G^{\circ}_{\mathrm{H}^-}$values, or hydride transfer potentials, parallels the $E_{1/2}$ values for the (II/0) couples, but the order does not follow the sequence of $\mathrm{p}K_{\mathrm{H}^+}$ values. More electron-donating substituents increase the hydride donor potential (lower $\Delta G^{\circ}_{\mathrm{H}^-}$values) with Me > Et > Ph. For example, $[\mathrm{HNi(dmpe)_2}]^+$ and $[\mathrm{HPt(dmpe)_2}]^+$ are approximately 14 kcal $\mathrm{mol^{-1}}$ better hydride donors than $[\mathrm{HNi(dppe)_2}]^+$ and $[\mathrm{HPt(dppe)_2}]^+$ respectively. For the same diphosphine ligand, platinum is a 10 to 15 kcal $\mathrm{mol^{-1}}$ better hydride donor than nickel. A smaller chelate bite also appears to favor hydride transfer, because the hydride donor abilities of $[\mathrm{HNi(dmpe)_2}]^+$ and $[\mathrm{HPt(dmpe)_2}]^+$ are approximately 10 kcal $\mathrm{mol^{-1}}$ greater than those of $[\mathrm{HNi(dmpp)_2}]^+$ and $[\mathrm{HPt(dmpp)_2}]^+$ respectively. Of the complexes studied, the best hydride donor is $[\mathrm{HPt(dmpe)_2}]^+$, a third-row metal complex containing a diphosphine ligand with a small chelate bite and electron-donating methyl groups.

The best hydride acceptors have the opposite characteristics. From Table 1 it appears that $[\mathrm{Ni(dppe)_2}]^{2+}$ and $[\mathrm{Ni(dmpp)_2}]^{2+}$ should be the best hydride acceptors based upon $\Delta G^{\circ}_{\mathrm{H}^-}$.To evaluate the ability of these complexes to act as hydride acceptors, we studied the reaction of $[\mathrm{Ni(dppe)_2}]^{2+}$ and $[\mathrm{Ni(dmpp)_2}]^{2+}$ with hydrogen in dimethylformamide. It was observed that $[\mathrm{Ni(dmpp)_2}]^{2+}$ heterolytically cleaves hydrogen to form $[\mathrm{HNi(dmpp)_2}]^+$. In this case the metal complex is a sufficiently good hydride acceptor that it can cleave the H—H bond, and the reaction illustrates the usefulness of the free energy data shown in Table 1 for predicting feasible reactions. However, $[\mathrm{Ni(dppe)_2}]^{2+}$ does not react with hydrogen under the same conditions, which implies there is a kinetic constraint for this complex.

Comparison of the $[\mathrm{HM(diphosphine)_2}]^+$ complexes with the $\mathrm{CpM(CO)_2(L)H}$ complexes (M = Mo or W) studied by Sarker and Bruno[6] is instructive. For $\mathrm{CpMo(CO)_3H}$ and $\mathrm{CpMo(CO)_2(PMe_3)H}$ the values of $\Delta G^{\circ}_{\mathrm{H}^-}$were found to be

88.6 kcal mol^{-1} and 79.4 kcal mol^{-1} respectively, with a lower value representing a better hydride donor. It is clear that the $[HM(diphosphine)_2]^+$ complexes in Table 1 are much more powerful hydride donors than the molybdenum hydride complexes. $[HNi(dppe)_2]^+$, the poorest hydride donor in our study, is a stronger hydride donor by approximately 16 kcal mol^{-1} than $CpMo(CO)_2(PMe_3)H$, the best hydride donor in the $CpM(CO)_2(L)H$ series; and $[HPt(dmpe)_2]^+$ is a stronger hydride donor by 40 kcal mol^{-1}. These data emphasize the important role of the stability of the unsaturated complexes that result from hydride transfer. For the $[HM(diphosphine)_2]^+$ complexes, stable square-planar complexes are formed. This feature appears to be more important than the charge on the hydride complexes or the position of the transition metal in the Periodic Table.

The reactivity of $[HM(diphosphine)_2]^+$ complexes with $[CpRe(CO)_2NO]^+$ to form the corresponding formyl complex, reaction [2], parallels the hydride donor abilities. For example, $[HPt(dmpe)_2]^+$, $[HPt(depe)_2]^+$, and $[HNi(dmpe)_2]^+$ react with $[CpRe(CO)_2NO]^+$, but complexes less hydridic than $[HNi(dmpe)_2]^+$ do not react to form the formyl complex. Similarly, $[HPt(dmpe)_2]^+$ and $[HPt(depe)_2]^+$ react with CO_2 in acetonitrile to form formate, but less hydridic complexes do not. In fact formate can be used to reduce $[Pt(dmpp)_2]^+$ to form $[HPt(dmpp)_2]^+$. These results indicate the hydride donor ability of formate and $[HPt(depe)_2]^+$ are comparable. This is supported by the observation that formate reduces the $[M(diphosphine)_2]^{2+}$ above $[HPt(depe)_2]^+$ in Table 1. Thus a quantitative understanding of the hydride donor abilities of the $[HM(diphosphine)_2]^+$ complexes is extremely useful in understanding and predicting hydride transfer reactions to CO_2 and coordinated CO.

SUMMARY

Very fast, selective, and energy efficient electrocatalysts have been developed for the electrochemical reduction of CO_2 to CO. This reaction involves a migration of water or hydroxide from carbon to palladium, and it requires a vacant coordination site on the catalyst. Initial work on CO reduction has demonstrated that electrochemically generated hydrides can reduce coordinated CO to formyl ligands. A thermochemical cycle has been used to measure the relative hydride donor abilities of a series of $[HM(diphosphine)_2]^+$ complexes. For the $[HM(diphosphine)_2]^+$ cations, the features favoring hydride donation are a third-row transition metal containing a diphosphine ligand with basic substituents and a small chelate bite. These are the same factors that promote transfer of the hydride ligand from these complexes to CO_2 and coordinated CO.

EXPERIMENTAL

Hydrogen activation

These reactions were performed by dissolving 20–30 mg of $[M(L)_2]^{2+}$ (M = Ni, Pt; L = dmpe, depe, dmpp) in dimethylformamide-d_7 (0.7 ml) and bubbling hydrogen through the solution. The reactions were monitored by ^{31}P and ^1H NMR spectroscopy.

CO_2 reduction

These reactions were performed by dissolving 20–30 mg of $[HM(L)_2]^+$ (M = Ni, Pt; L = dmpe, depe, dmpp) in acetonitrile-d_3 (0.7 ml) and bubbling CO_2 through the solution. The reactions were monitored by ^{31}P and ^1H NMR spectroscopy.

Formate oxidation

These reactions were performed by dissolving 20–30 mg of $[M(L)_2]^{2+}$ (M = Ni, Pt; L = dmpe, depe, dmpp) in acetonitrile-d_3 (0.7 ml) and adding an equivalent weight of NBu_4HCOO. The reactions were monitored by ^{31}P and ^1H NMR spectroscopy.

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