hydrogen gases were evolved. This leads to the conclusion that the hydride and formate hydrogens in **2** originate exclusively from the hydride in **1** and that the methyl group maintains its integrity. Potential sinks for the methyl group other than those observed include methyl acetate for which there is ^{13}C NMR spectral evidence. Efforts are continuing to more fully characterize reaction 1, both chemically and mechanistically.

Whereas reductive elimination of CH_4 from **1** was readily induced by ambient lighting or by addition of a donor ligand such as CO, compound **2** was stable under these conditions.[12] In fact neither reductive elimination nor decarboxylation occurred after prolonged heating at 50 °C. Even so, when **2** is dissolved in benzene-d_6 under 1 atm $^{13}CO_2$, carbon dioxide is incorporated as shown in eq 3. At 22 °C the half-life for this reaction is about 150 min.

$$(Cy_3P)_2Ni(H)(O_2CH) + {}^{13}CO_2 \rightleftarrows (PCy_3)_2Ni(H)(O_2{}^{13}CH) + {}^{12}CO_2 \quad (3)$$

The preparation of **2-d_1**, from the reaction of $\{(Cy_3P)_2Ni\}_2N_2$ and HCOOD,[13] permitted a study of the rate of the exchange process described in eq 4. Interestingly, this equilibrium between

$$\underset{\textbf{2-}d_1}{(Cy_3P)_2Ni(D)(O_2CH)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\textbf{2-}d'_1}{(PCy_3)_2Ni(H)(O_2CD)} \quad (4)$$

2-d_1 and **2-d'_1** was achieved in the solid state after ca. 7 days. When in solution the equilibrium is attained with an equal distribution of deuterium between hydride and formate positions. The reaction is first-order in complex **2** with a $t_{1/2}$ for progress toward equilibrium of 510 min. Since both $^{13}CO_2/CO_2$ exchange in (3) and H/D exchange in (4) may proceed by way of CO_2 extrusion and a $Ni(H)_2$ intermediate, it is possible that the two reactions are related. It has not been possible to prepare the dihydride species from $[(Cy_3P)_2Ni]_2N_2$ and H_2; however, alternative synthetic routes to this species are being pursued.[14] At this juncture it is not clear that the difference in rates of reactions of eq 3 and 4 is due to a kinetic isotope effect or to a difference in reaction pathway, although preliminary experiments are supportive of the former. Consistent with this interpretation, decarboxylation of the analogous *trans*-$PtH(O_2CH)(PEt_3)_2$ derivative affords the stable $PtH_2(PEt_3)_2$ species plus carbon dioxide.[15] Detailed kinetic and mechanistic investigations addressing this issue are in progress.

Despite the complex nature of the reaction of **1** with CO_2, the analogous $HNi(Ph)(PCy_3)_2$ species undergoes simple CO_2 insertion into the Ni–H bond to quantitatively yield $HCO_2Ni(Ph)(PCy_3)_2$. This is an important observation in that Pd(II) phosphine complexes, known to react with benzene to provide H–Pd–Ph species,[16] have been reported to catalyze the production of benzoic acid from benzene and carbon dioxide.[17] Common proposed cycles for this process include either a phenylmetallocarboxylic acid, HOOC–Pd–Ph, or a hydridometalbenzoate, H–Pd–O_2CPh, as proposed intermediates. The contrasting results of the above nickel study are, in fact, more consistent with literature precedents and suggest that alternate pathways might be available for the Pd-catalyzed carboxylic acid synthesis.

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 86-03681 DJD) and (Grant CHE 86-03664 MYD) is greatly appreciated. In addition we acknowledge with thanks financial support by the Board of Regents of Texas A&M University.

Supplementary Material Available: A listing of rate data and plots of H/D exchange in $DNi(O_2CH)(Cy_3P)_2$ (2 pages). Ordering information is given on any current masthead page.

(12) Formic acid is eliminated from **2** upon addition of the oxidative exchange reagent, $(p\text{-TolS})_2$, yielding $[(PCy_3)Ni(S\text{-}p\text{-Tol})_2]_2$. Darensbourg, M. Y.; Ludvig, M., unpublished results.

(13) $[Ni(PCy_3)_2]_2N_2$ (1.54 g) dissolved in 25 mL of toluene was purged with argon until the solution turned yellow in color. The volume was reduced to approximately 7 mL followed by addition of a preequilibrated solution of 0.22 mL D_2O/0.092 mL HCO_2H in 15 mL of Et_2O. The resulting yellow product was isolated by filtration and dried in vacuo (1.40 g, 87% yield). ^2H NMR: −27.51 ppm (t), J_{PH} = 11.09 Hz. ^1H NMR: 8.91 ppm.

(14) The instability of the dihydride was noted earlier from attempts to prepare $(Cy_3P)_2Ni(Et)H$.[4] In that work H_2 evolved, presumably via β-elimination of the desired complex, yielding $(C_2H_4)Ni(PCy_3)_2$. Nevertheless, in the cold and in the absence of a displacing ligand, the $(Cy_3P)_2Ni(H)_2$ complex might have an appreciable lifetime.

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Electron Transfer in the Cytochrome *c*/Cytochrome b_2 Complex: Evidence for "Conformational Gating"

George McLendon,* Kelli Pardue, and Phillip Bak

Department of Chemistry, University of Rochester Rochester, New York 14627

Received May 18, 1987

Since long distance electron transfer between proteins controls the flow of biological energy, the factors which control these rates remain a subject of intense continuing interest.[1-3] Over the last few years, research ranging from model systems[4-8] to natural protein complexes has shown that in general, such rates are characterized by a strong ($\sim$ exponential) dependence on distance[1,4] and also by a strong dependence on reaction free energy[1-12] as embodied in Marcus theory.[1] Although most theoretical treatments assume that the configurational changes which accompany electron transfer (e.g., solvent repolarization) occur rapidly, this is not universally true.[13-16] In particular, Hoffman

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(15) In independent work we have established the redox potentials of Zn cytochrome *c* and porphyrin cytochrome *c* by cyclic voltammetry $E°_{Znc}$ = 0.85 $E°_{porph\ c}$ = 1.05 including the triplet state energies $^3(Znc)$ = 1.6_5 (porph *c*) = 1.4_5 gives $E°_{(Zn/Zn^+)}$ = 0.8_4 $E°_{(^3porph/porph)^+}$ = 0.40. Details of this work will be presented elsewhere (Magner, E.; McLendon, G., submitted for publication).

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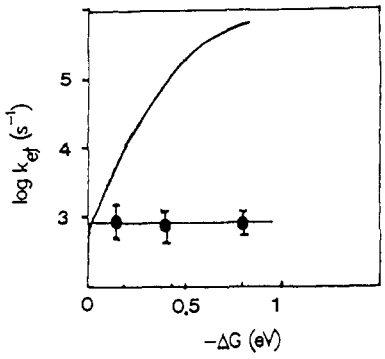

Figure 1. Plot of b_5 K_{et} vs $-\Delta G$ for the intra complex electron transfer between b_2 and (M)cytc where M = Fe(III) ^{3}(Zn*), ^{3}(porph*). The top solid line shows the dependence predicted by Marcus theory (for $\lambda \sim 1$ V, as e.g., in cytochrome c/cytochrome b_5): conditions pH 7 (5 mM Pi), 25 °C.

and Ratner have recently argued that for proteins, redox linked configurational changes may well be rate limiting.[15] In such cases, the familiar dependence of rate on reaction free energy would not hold. We now present evidence for such "conformational gating"[15] in the reaction of cytochrome c (c) with cytochrome b_2 (b_2) (yeast lactate dehydrogenase). This system is of special interest for several reasons. First the b_2/c system has been the subject of long standing elegant studies by Labeyrie and co-workers.[12,16] Second, the structure of b_2 has recently been solved by Matthews,[17] and the prospect exists of obtaining a detailed structure for the complex.[16] Finally, well characterized metal substituted cytochrome c derivatives are available, so that ΔG can be easily varied in the c/b_2 complex.[9] Cytochrome c and the derivatives H_2 porphyrin cyctochrome c (porph c) and Zn(II) cytochrome c (Znc) were prepared and purified as previously described.[9,15] Cytochrome b_2 was purified from *Saccaromyces cervisiae*, as described previously.[18] Electron transfer within the preformed $Fe^{II}c/Fe^{III}b_2$ complex has been previously studied in two labs. Capelliere Blandin used stopped flow techniques to measure a rate constant of 380 s^{-1} at 5 °C between *H. anomola* cytochrome b_2^{II}/cytochrome c^{III}. With use of the reported activation energy (3.3 Kcal M^{-1}), the rate constant at 25 °C would be 570 s^{-1}. For horse cytochrome c, the rate is reported to decrease about fourfold.[11b]

In the present work we have used the lumiflavin chemistry pioneered by Tollin and Cusanovich[9c] to photochemically reduce cytb_2 and follow electron transfer within a preformed (horse) c/b_2 complex and find a rate constant of 200 ± 80 s^{-1} under our conditions (25 °C, pH 7, 5 mMPi) in reasonable agreement with previous work. Thus, while the rate of intracomplex electron transfer is sensitive to the primary sequence of the protein and perhaps to specific solution conditions as well, a range of rates of 600 ± 300 s^{-1} encompass all these variations for the native $Fe^{II}b_2/Fe^{III}c$ reaction. In order to better characterize the parameters which control electron transfer in the cyt$c$/cytb_2 system, we have utilized redox photoactive derivatives[9,10] (e.g., Znc) which provide a range of reaction free energies: for the porphc/b_2 complex $\Delta G \cong -0.4$ V, for the Znc/b_2 complex $\Delta G \cong 0.8$ V. As discussed in detail elsewhere,[9-11] the Znc and porph$c$ derivatives are essentially isostructural with the native cytochrome c. They form strong, specific complexes with cytochrome b_2, as shown by fluorescence energy transfer experiments.[11] Furthermore, both Znc and porph$c$ act as strong competitive inhibitors in steady-state enzyme assays of the lactate/b_2/Fec reaction:[11a] for Znc we find $K_I \cong K_m \cong 10$ μM. The available evidence thus suggests that Fec, Znc, and porph$c$ all form equivalent complexes with cytochrome b_2 and the electron-transfer rates among these complexes should proceed by similar mechanisms. Both theory and previous experimental results on other protein complexes suggest that the large change in ΔG between b_2/Fec and b_2/Znc should result in correspondingly large differences in electron-transfer rates. To our surprise, and in contrast to other protein systems,[7,9,10] reaction rates for these c/b_2 complexes are essentially *independent* of ΔG over this wide range (Figure 1: k_{Zn/b_2} = 600 (± 200) s^{-1}, k_{porph/b_2} = 700 (±100) s^{-1})!

We believe these results offer compelling support for the importance of conformational control of reaction rates, in a complex formed between physiological protein reactants. In the "gating" mechanism proposed by Hoffman and Ratner,[16] the overall reaction rate can be controlled by the rate of formation of "redox active" conformation within the complex, and this need not depend on those factors like free energy and electronic coupling of strengths which normally govern electron transfer rates. The current results are fully consistent with this theory.[20] We note that the existence of such conformational "upper limits" to reaction may exist even when a normal dependence of rate or free energy is observed, as in the cytochrome c/cytochrome b_5 complex,[9] which could lead to lower overall rates than would be expected in the absence of such conformational barriers. The source of such conformational barriers remains unclear. We are currently undertaking studies by using site directed mutagenesis to help clarify this and related questions.

Acknowledgment. This work was supported by the NIH (GM33881) and in part by the NSF (CHE8303896). We gratefully acknowledge helpful discussions with Brian Hoffman, Mike Cusanovich, Chantal Cappelliere Blandin, and Harry Gray.

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Trinitrosyl Species on Supported Iron Catalysts

B. A. Morrow,* M. I. Baraton,† and J.-L. Roustan*

Department of Chemistry, University of Ottawa
Ottawa, Ontario, Canada K1N 6N5
Received July 27, 1987

Nitric oxide has frequently been used as a probe molecule for assessing the adsorbed state of catalytically active metallic species on the surface or in the bulk of oxides and zeolites.[1] In the case of cobalt[2-9] and iron,[10-13] a pair of infrared bands near 1900 cm^{-1}

†On leave from Laboratoire de Spectroscopie, Faculté des Sciences, Limoges, France.
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