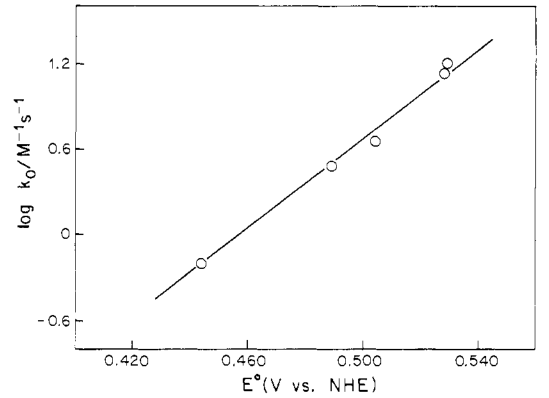

Figure 1. Correlations of NADH and **1** rate constants with **1/2** equilibrium constants.

reacting 4–8 mM NADH with 0.2–0.4 mM **1a**. NADH was always in at least 20-fold excess so that pseudo-first-order kinetics were observed. Rate constants were calculated from the measured decay of the absorption of **1a** at 618 nm. The reaction was found to be first order in NADH and first order in **1a**. The observed rate constants were independent of the pH in the range of pH 6–9. There was also no change in rate when [4-^{1}H,4-^{2}H]NADH[8] was reacted with **1a**. All of these results are consistent with rate-limiting electron transfer from NADH to **1a** according to Scheme I.

Rate constants were similarly determined for the other ferrocenium oxidants **1**. From data obtained at several concentrations, it was found in each case that the kinetics were strictly second order overall. As indicated by the data in Table I, the observed rate constants changed when the salt concentration was varied. Rate constants were, therefore, determined at several concentrations of $NaClO_4$ for each of the ferrocenium cations investigated. The rate constants were then extrapolated to zero salt concentration to give k_0, the rate constant in the absence of $NaClO_4$. The results are in Table II. All of the measured rate constants for each reactant **1** were reproducible to ±5% or better.

The electrochemical $E^{\circ\prime}$ values of the ferrocene/ferrocenium couples were determined by cyclic voltammetry in the same solvent as was used for the kinetic experiments.[9] A salt effect was again observed and the $E^{\circ\prime}$ values were extrapolated to zero $NaClO_4$ concentration. For the five ferrocenium cations investigated log k_0 was then plotted against $E^{\circ\prime}$ (Figure 1). A linear plot (r = 0.998) was observed with a slope of 16.0 V^{-1}. This is in good agreement with the value of 16.6 V^{-1} expected[10] at 30 °C for an endothermic rate-limiting electron transfer followed by rapid deprotonation of $NADH^{+\cdot}$ by a base.[11]

The $E^{\circ\prime}$ for the $NADH/NADH^{+\cdot}$ couple can be determined by extrapolating the log k_0 value up to the diffusion-controlled rate limit in the solvent system being used.[10c] Assuming $k_{diff} = 3 \times 10^9$ M^{-1} s^{-1}, this plot yields a value of 1.05 V vs. NHE. This is the first determination of this $E^{\circ\prime}$ value for NADH in an aqueous system. The value can be compared with the $E^{\circ\prime}$ = 1.00 V estimated for 1-benzyl-1,4-dihydronicotinamide in acetonitrile[12] where quenching of electronically excited dihydronicotinamide was used for the determination.

The rates reported here allow one to calculate certain rate constants for one-electron transfer from NADH. Such calculations can in principle lead to the critical evaluation of proposed mechanisms for chemical and electrochemical NADH oxidations, especially those in which electron transfer is the initial step.[2d,e4,13] In a future paper these evaluations will be performed. For the present we simply emphasize that we have been able to design an authentic example of an NADH oxidation with rate-controlling one-electron transfer. The data demonstrate that because the $E^{\circ\prime}$ for $NADH/NADH^{+\cdot}$ is so positive, rather powerful one-electron oxidants are required to enter this mechanistic manifold.

Acknowledgment. This work was supported by the National Science Foundation. Stimulating conversations with J. M Dumas-Bouchiat and P. Neta are alsö acknowledged.

Registry No. 1 (R = HgCl; R′ = H), 34742-71-7; **1** (R = Bu; R′ = H), 33306-90-0; **1** (R = Et; R′ = H), 12276-62-9; **1** (R = Me; R′ = Me), 12276-63-0; **1a**, 12125-80-3; NADH, 58-68-4.

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[8] The NADH was stereospecifically labeled with deuterium in the *pro-R* position. The lack of an observable isotope effect is surprising as a secondary isotope effect on the rate of electron transfer might be expected. The isotope effect on this and similar reactions will be investigated further.

[9] The values obtained are in satisfactory agreement with several that were previously reported. Pladziewicz, J. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 56.

[10] (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Eberson, L. "Advances in Physical Organic Chemistry"; Academic Press: New York, 1982; Vol. 18, p 79. (c) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; Saveant, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 3431.

[11] Theory predicts that the overall electron transfer is composed of three processes: diffusion together, electron hop, and diffusional separation. The slope of 16.0 V^{-1} suggests that diffusional separation limits the rate of formation of $NADH^{+\cdot}$.

[12] Martens, F. M.; Verhoeven, J. W.; Gase, R. A.; Pandit, U. K.; de Boer, T. J. *Tetrahedron* **1978**, *34*, 443.

[13] (a) Land, E. J.; Swallow, A. J. *Biochim. Biophys. Acta* **1971**, *234*, 34. (b) Bielski, B. H. J.; Chan, P. C. *Arch. Biochem. Biophys.* **1973**, *159*, 873. (c) Blankenhorn, G. *Eur. J. Biochem.* **1976**, *67*, 67. (d) Okamoto, T.; Ohno, A.; Oka, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 330. (e) Yasui, S.; Nakamura, K.; Ohno, A.; Oka, S. *Ibid.* **1982**, *55*, 196; (f) Moiroux, J.; Elving, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 6533. (g) Kitani, A.; Miller, L. L. *Ibid.* **1981**, *103*, 3595.

Neutralization–Reionization Mass Spectrometry (NRMS)

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Reionization of neutral products of gaseous ion decompositions has been achieved by collisional activation;[1,2] the resulting mass spectra appear useful for characterizing these neutrals. Porter and co-workers[3] have generated unstable neutral species such as NH_4 and CH_5 by neutralization of the corresponding ions, measuring the energy released in dissociation to characterize the neutrals. We report here that combining neutralization and reionization[4] in tandem mass spectrometry[5] can provide valuable new information on the structures and chemistry of (a) such neutrals, (b) ions, and (c) normal molecules.

In NRMS the appropriate precursor ion of multikilovolt kinetic energy is generated and mass selected in the first mass spectrometer (MS-I).[6] From this ion the desired neutral is produced by charge exchange with an appropriate metal vapor[3] or by metastable or collisionally activated dissociation (CAD).[7] Residual ions are deflected electrostatically from the resulting beam of fast neutrals, which is then ionized[1] by collision with a neutral

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[1] McLafferty, F. W.; Todd, P. J.; McGilvery, D. C.; Baldwin, M. A. *J. Am. Chem. Soc.* **1980**, *102*, 3360–3363.

[2] Also by electron ionization using ion cyclotron resonance: Lieder, C. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1974**, *96*, 4028.

[3] Williams, B. W.; Porter, R. F. *J. Chem. Phys.* **1980**, *73*, 5598. Cleary, D. A.; Gellene, G. I.; Porter, R. F.; Burkhardt, C. E.; Leventhal, J. J. *Ibid.* **1982**, *77*, 1354. Gellene, G. I.; Porter, R. F. *Acc. Chem. Res.* **1983**, *16*, 200.

[4] Neutralization of ions (not mass selected) followed by reionization has provided energy-level information on monoatomic ions: Durup, M.; Parlant, G.; Appell, J.; Durup, J.; Ozenne, J.-B. *Chem. Phys.* **1977**, *25*, 245.

[5] McLafferty, F. W. *Science (Washington, D.C.)* **1981**, *214*, 280–287.

[6] The previous instrumentation[1] was used with an electrostatic sector as MS-II. A metal-vapor furnace was placed between the MS-I exit and the ion lens preceeding the beam collision region. The distance between neutralization and reionization is 18 cm, flight time ~10^{-6} s.

[7] McLafferty, F. W.; Bente, P. F., III; Kornfeld, R.; Tsai, S.-C.; Howe, I. *J. Am. Chem. Soc.* **1973**, *95*, 2120.

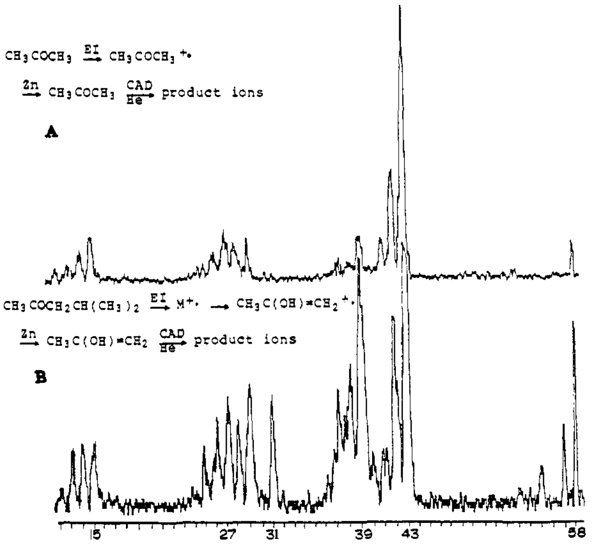


Figure 1. NR mass spectra[6] of (A) acetone (ionization energy, 9.6 eV) and (B) its enol (9.2 eV) from neutralization of the corresponding ions with Zn (9.4 eV) and reionization by CAD with He.

target gas. Product ions formed with sufficient energy undergo further dissociation, so that scanning MS–II produces a characteristic CAD mass spectrum of the neutrals. That of acetone (Figure 1A) is surprisingly similar to its normal electron ionization (EI) mass spectrum.[8]

Unstable and reactive neutrals can be generated by NRMS from a corresponding ionic form which is stable. Formation of the neutral enol of acetone from its cation gives the NR mass spectrum of Figure 1B. The larger (vs. Figure 1A) *m/z* 58 is consistent with the relative stability of the molecular ions,[9] not their neutrals, indicating that most of the fragmentation occurs after reionization. The *m/z* 31 is typical of EI mass spectra of alcohols.[10]

Not surprisingly, dissociation after neutralization[11] is extensive for the previously unknown $HClCH_2$, the ylide isomer of methyl chloride (Figure 2). This structure is predicted from that of its ionic precursor $HClCH_2^{+\cdot}$[12] and similar species[12,13] and confirmed by NRMS of $DClCH_2$, whose dissocation (Figure 2C) yields predominantly DCl, not HCl, and $ClCH_2\cdot$, not $ClCHD\cdot$. Consistent with lower stability, $HClCH_2$ yields a $M^{+\cdot}$:$HCl^{+\cdot}$ ratio of 0.2,[14] while that from $ClCH_3$ is 5. The internal energy of the neutral formed can be lowered by neutralization with Hg, ionization energy (IE) 10.4 eV, instead of Zn (9.4 eV);[3] this raises $M^{+\cdot}$:$HCl^{+\cdot}$ for $ClCH_3^{+\cdot}$ to 18 and that for $HClCH_2^{+\cdot}$ to 1.2. The latter $M^{+\cdot}$ (*m/z* 52) abundance indicates, but does not prove,[15] that some $HClCH_2$ molecules have survived for $\sim 10^{-6}$ s. We plan to use NRMS to examine other unstable neutrals formed from stable ions, such as cyclobutadiene from $C_4H_4^{2+}$, reaction transition states, and hypervalent species.[3,16]

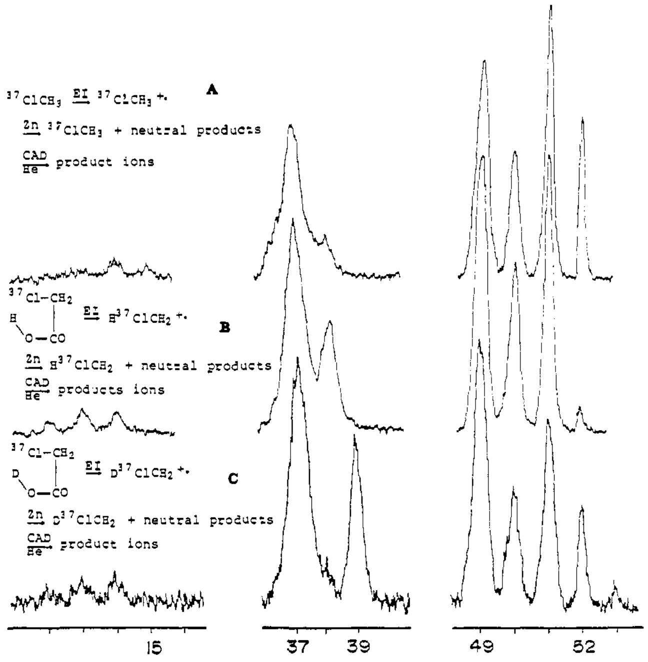
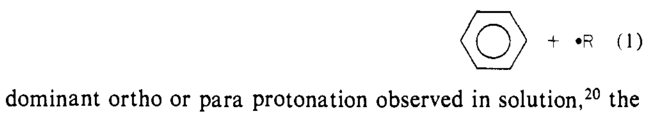


Figure 2. NR mass spectra of (A) $^{37}ClCH_3$ (IE, 10.6 eV), (B) $H^{37}ClCH_2$, and (C) $D^{37}ClCH_2$.

Ion Structures. The NR mass spectra of Figures 1 and 2 also provide persuasive evidence that these originate from different isomeric ions. NRMS can also differentiate ions on the basis of their electron affinity (EA, the IE of the corresponding neutral). Although isomeric butyl ions show nearly identical CAD mass spectra,[17] neutralizing these with Mg (IE = 7.6 eV) yields NR mass spectra for the *n*-, *i*-, and *sec*-$C_4H_9^+$ isomers[18] (EA = 8.0, 8.0, and 7.4 eV, respectively), but not (<1% of *sec*-$C_4H_9^+$) for *t*-$C_4H_9^+$ (6.7 eV).

Neutralization of an ion can also make possible a dissociation pathway more definitive for structure determination. The site of gaseous protonation in alkylbenzenes could not be defined from conventional CAD spectra, as the RC_6H_5–H^+ ions from ipso and ortho or para protonation gave similar spectra.[19] However, dissociation of the corresponding neutral isomers to yield aromatic molecules (eq 1) should be more selective. Consistent with the dominant ortho or para protonation observed in solution,[20] the NR mass spectrum of the $C_7H_9^+$ ions from protonation (chemical ionization) of toluene shows insignificant (≤5%) CH_3 and C_6H_6 peaks and is closely similar to the NR spectrum from ionized toluene.



(1)

Molecular Structures. Electron (EI) and chemical (CI) ionizations initially form, respectively, odd-electron ($OE^{+\cdot}$) and even-electron (EE^+) ions. Dissociation of OE^{+}.· ions produces both $OE^{+\cdot}$ and EE^+ fragment ions, while dissociation of EE^+ ions yields mainly EE^+ fragments by less specific pathways.[10,21]

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[8] Stenhagen, E.; Arabamsson, S.; McLafferty, F. W. "Registry of Mass Spectra Data"; Wiley-Interscience: New York, 1974.

[9] Bouma, W. J.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1977**, *99*, 6643. Holmes, J. L.; Lossing, F. P. *Ibid.* **1980**, *102*, 1591.

[10] McLafferty, F. W. "Interpretation of Mass Spectra"; 3rd ed.; University Science Books: Mill Valley, CA, 1980.

[11] Kinetic energy released in neutral dissociation causes an angular displacement of the products.[3] We plan to obtain NR spectra as a function of this angle to distinguish fragments of the neutrals from those formed after CAD ionization.

[12] Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 2931. Terlouw, J. K.; Heerma, W.; Dijkstra, G.; Holmes, J. L.; Burgers, P. C. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *47*, 147.

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[14] Subtracting out contributions of neutral dissociation products on the basis of their reference NR spectra indicates that >70% of $H^{37}Cl$ in Figure 2B comes directly from $HClCH_2$.

[15] These ions could be $ClCH_3^{+\cdot}$; their structure may be determinable from another CAD spectrum[12] measured with the final magnet.[1]

[16] Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54; Forbus, T. R.; Jr.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5057.

[17] Dymerski, P. P; McLafferty, F. W. *J. Am. Chem. Soc.* **1976**, *98*, 6070.

[18] These spectra, and CAD spectra from reionization of $C_4H_9\cdot$ isomers from metastable decomposition of $C_6H_5NHCH_2C_4H_9$, will be compared in the full paper.

[19] Gross, M. L.; Miller, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 3783.

[20] Smith, B. V. In "Organic Reaction Mechanism"; Butler, A. R., Perkins, M. J., Eds.; Wiley: New York, 1976; p 299.

[21] McLafferty, F. W. *Org. Mass Spectrom.* **1980**, *15*, 114–121.

However, neutralization of an EE^+ produces an $OE^{\circ}\cdot$ neutral, which should undergo specific "radical site" dissociations.[10,22] For example, CI of CH_3OH yields $CH_3OH_2^+$, whose neutralization (Hg) produces the hypervalent[16] $CH_3\dot{O}H_2$. This NR spectrum shows the expected dissociation to $\cdot CH_3$ to H_2O. The most abundant ion not formed by H losses is $H_2O^{+\cdot}$;[23] EI mass spectra do not give such a direct characterization of the hydroxyl group. For many compounds CI can produce mainly $(M + H)^+$; here the NR mass spectrum could provide structure information without mass selecting $(M + H)^+$, i.e., CI-NR followed by a normal mass spectrometer. Reionization of the neutral product of an ionic dissociation can also provide structural information.[1] Metastable aniline ions lose $C_5H_6^+$ producing HNC,[24] as shown by their CAD spectrum: *m/z* 26:27 = 0.8; NRMS (Hg) of HNC^+,[25] 0.8, and of HCN^+, 1.5.

Acknowledgment. P. J. Todd, R. F. Porter, G. I. Gellene, B. K. Carpenter, and M. and J. Durup provided helpful advice and R. Feng valuable experimental assistance. The National Institutes of Health (Grant GM16609) and the Army Research Office, Durham (Grant G29-79-C-0046), furnished financial support.

Registry No. $ClCH_2\cdot$, 6806-86-6; *n*-$C_4H_9^+$, 25453-90-1; *i*-$C_4H_9^+$, 19252-54-1; *sec*-$C_4H_9^+$, 16548-59-7; *t*-$C_4H_9^+$, 14804-25-2; CH_3OH, 67-56-1; $CH_3\cdot$, 2229-07-4; Hg, 7439-97-6; methyl chloride, 74-87-3; toluene, 108-88-3; monoprotonated toluene, 52809-63-9; magnesium, 7439-95-4; water, 7732-18-5.

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[22] Huyser, E. S. In "Organic Reactive Intermediates"; McManus, S. P., Ed.; Academic Press: New York, 1973; Vol. 26, p 1.

[23] The counterpart product $\cdot CH_3$ is indicated by $CH_3^{+\cdot}$. In contrast, in EI spectra a counterpart product is negligible if it has a much higher ionization energy (Stevenson's Rule).[10]

[24] Lifshitz, C.; Gotchiguian, P.; Roller, R. *Chem. Phys. Lett.* **1983**, *95*, 106.

[25] McLafferty, F. W.; McGilvery, D. D. *J. Am. Chem. Soc.* **1980**, *102*, 6189.

Electrocatalytic Oxidation of Carbon Monoxide in a CO/O_2 Fuel Cell

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We report the electrocatalytic oxidation of carbon monoxide in a low-temperature CO/O_2 fuel cell using a homogeneous electrocatalyst. The CO/O_2 fuel cell represents the most efficient potential means of converting chemical energy in the form of CO and O_2 to electrical energy. The overall fuel cell reaction (eq 1)

$$CO + {}^1/_2O_2 \rightleftharpoons CO_2 \qquad E^\circ = 1.33\text{ V} \qquad (1)$$

has a higher expected output, 1.33 V, than the more familiar H_2/O_2 cell. The CO/O_2 cell is also attractive since CO may be obtained from coal gas directly. The efficiencies for CO/O_2 fuel cells, however, have been severely limited by the kinetic inertness of CO and by the attendant rapid polarization and poisoning of most electrode materials.[1,2] Overpotentials, V_{op}, for the oxidation of CO to CO_2 at conventional electrode materials such as platinum and graphite typically are found to be >1.25 V. Recently, heterogeneous electrocatalysts for CO oxidation based on carbon-supported metalloporphyrins have been reported.[3,4] We now describe a homogeneous rhodium-based electrocatalyst that promotes efficient electrochemical oxidation of CO to CO_2 in acidic solutions. The design and output characteristics of prototypal fuel cells that employ the new electrocatalyst are also described.

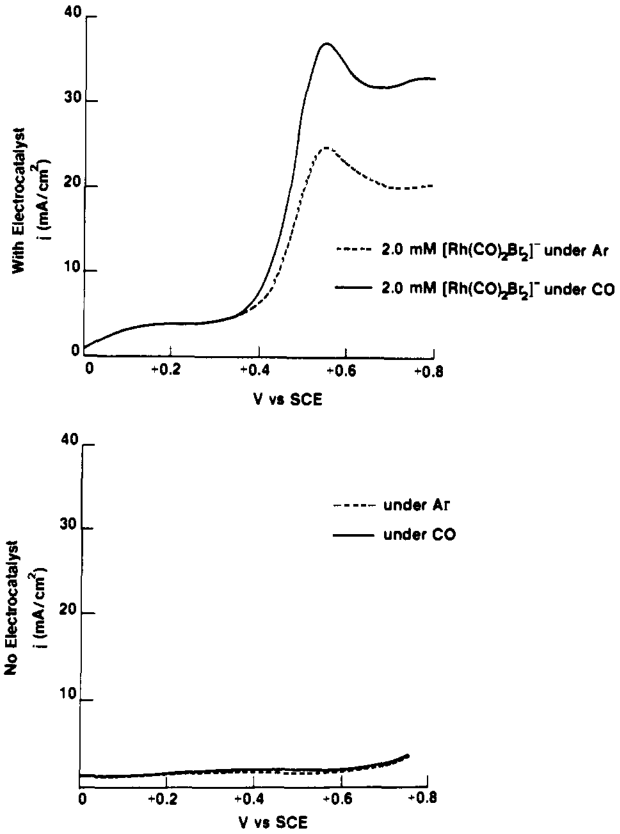

Figure 1. The oxidation of CO in 0.1 M HBr at a glassy carbon electrode (GCE) in the presence and absence of $[Rh(CO)_2Br_2]^-$ homogeneous electrocatalyst.

Acidic HX (X = Cl, Br, I) solutions of Rh^{III} are well-known to react with CO giving reduction to the formally Rh^I complexes[5-10] $[Rh^I(CO)_2X_2]^-$.[11-14] The reduction of Rh^{III} to Rh^I has been shown to result from nucleophilic attack of H_2O at a CO molecule coordinated to Rh^{III}.[15] The homogeneous oxidation of CO by Rh^{III} complexes has been a key feature of several catalytic reactions, notably the reduction of NO to N_2O by CO[15] and the water gas shift reaction.[16,17] We submit that favorable redox properties of $[Rh^I(CO)_2Br_2]^-$ with respect to the electrodic oxidation to Rh^{III} make these species electrocatalysts for the oxidation of CO to CO_2 at low overpotentials. In 0.1 M HBr solution, the onset for oxidation of $[Rh^I(CO)_2Br_2]^-$ is ~+0.40 V vs. SCE at a glassy carbon electrode (GCE). Controlled potential coulometry under Ar at +0.65 V. vs. SCE for the oxidation of $[Rh^I(CO)_2Br_2]^-$ gives 1.96 ± 0.08 F/mol Rh^I. The final product of the electrodic oxidation of $[Rh^I(CO)_2Br_2]^-$ in 0.1 M HBr is the Rh^{III} ion $[Rh^{III}(H_2O)_2Br_4]^-$, as confirmed by characteristic UV-vis absorptions at 537 (ϵ ~175) and 505 nm (ϵ ~150).[9] The reduction of $[Rh^{III}(H_2O)_2Br_4]^-$ by CO has been examined by James and Rosenberg[9] and leads to regeneration of $[Rh^I(CO)_2Br_2]^-$. These

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[1] See, for example: (a) Bockris, J. O. M.; Srinivasan, S. "Fuel Cells: Their Electrochemistry"; McGraw-Hill: New York, 1969. (b) Vielstich, W. "Fuel Cells"; Wiley-Interscience: New York, 1970.

[2] Bard, A. J. "Encyclopedia of Electrochemistry of the Elements"; Marcel Dekker: New York, 1976; Vol. VII, pp 153-154.

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