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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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)

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

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.

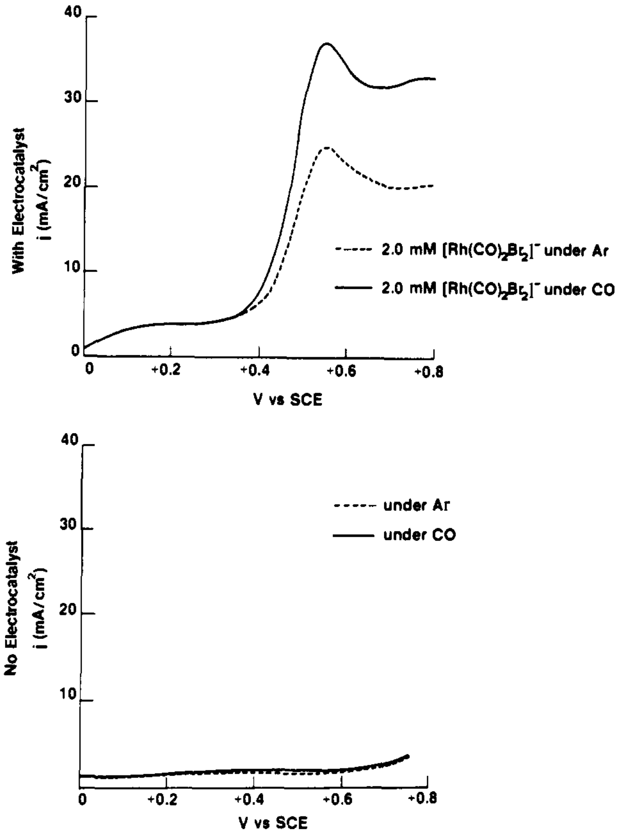

Figure 1. The oxidation of CO in 0.1 M HBr at a glassy carbon electrode (GCE) in the presence and absence of $[Rh(CO)_2Br_2]^-$ homogeneous electrocatalyst.

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.

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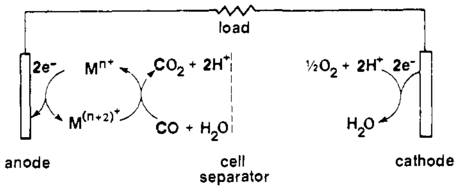
Scheme I. Generalized CO/O_2 Fuel Cell Employing the Two-Electron Redox Couple $M^{(n+2)/n+}$ of a Homogeneous Electrocatalyst[a]



[a] The maximum open circuit potential, V_{oc}, of such a cell is given by $V_{oc} = |E_{1/2}(M^{(n+2)+/n+}) - E_{1/2}(O_2/H_2O)|$.

results comprise a sufficient set of preconditions for the electrocatalytic oxidation of CO at potentials approaching +0.40 V vs. SCE. Results of steady-state i–V behavior of the electrochemical oxidation of CO in the presence and absence of $[Rh^I(CO)_2Br_2]^-$ at 25 °C are presented in Figure 1. The background current at a GCE in 0.1 M HBr under an Ar atmosphere (---) is shown at the bottom of the figure. When this same solution is saturated with CO (—), no discernible increase over background current is observed. We note that at these conditions the expected reversible potential for CO oxidation, $E°(CO_2/CO)$, is ∼−0.40 V vs. SCE. This result suggests that CO is not oxidizable at a GCE in 0.1 M HBr at potentials 1.20 V *more anodic* than expected from thermodynamic considerations alone. When $[Rh^I(CO)_2Br_2]^-$ is added to 0.1 M HBr solutions under Ar, the oxidation of Rh^I to Rh^{III} is evidenced, beginning at V ∼+0.40 V vs. SCE (---). When solutions of $[Rh^I(CO)_2Br_2]^-$ are placed under a CO atmosphere, a significant increase of ∼12 mA/cm^2 in anodic current densities associated with the oxidation of Rh^I is observed (—). This result suggests that in the presence of CO, Rh^{III} generated at the surface of a GCE can be reduced by CO and reoxidized at the electrode on a time scale that is faster than mass transport of Rh^I from the bulk solution. The complex $[Rh^I(CO)_2Br_2]^-$ is thus functioning as an electrocatalyst, mediating the oxidation of CO at potentials where no oxidation can be seen in its absence.

Rotating disk electrode (RDE) techniques[18] were used to determine the activation parameters for electrodic oxidation of $[Rh^I(CO)_2Br_2]^-$. At 25 °C the heterogeneous rate constant for the oxidation of $[Rh^I(CO)_2Br_2]^-$ at glassy carbon is $k^h = 1.86 \times 10^2$ cm s^{-1} in 0.1 M HBr.[19] The dependence of this rate constant on temperature has been examined over the range 25–55 °C, from which we find: $\Delta H^\ddagger = 4.87$ kJ mol^{-1} and $\Delta S^\ddagger = -16.8$ J mol^{-1} K^{-1}. The negative activation energy is consistent with the formation of a restricted activated complex at the electrode surface during oxidation. The small enthalpic term and negative entropic term underscore the advantage of electrocatalysts that can function at relatively low temperatures.

The electrocatalytic oxidation of CO by $[Rh^I(CO)_2Br_2]^-$ can be incorporated into laboratory-scale fuel cells of the general type shown in Scheme I. In these cells, the 2e⁻ CO/H_2O reducing equivalent is used to effect reduction of the oxidized form of the catalyst, $M^{(n+2)+}$, to M^{n+}, with concomitant CO_2 formation. In a separate step, the reduced form, M^{n+} is oxidized at an electrode, regenerating $M^{(n+2)+}$. The electrons released at the electrode are then available to sustain an electrical load and complete the cathodic process: reduction of O_2 to H_2O. The net chemical reaction is that of eq 1. We have examined the output characteristics of fuel cells designed as follows. A graphite anode is immersed in 40 mL of a 2.0 mM solution of $[Rh^I(CO)_2Br_2]^-$ in 0.1 M HBr. The anode compartment is charged with 1 atm of CO and connected to a GC gas-sampling loop. A Nafion 117 membrane separates the two cell compartments. The cathode compartment consists of a Pt gauze immersed in 0.1 M HBr solution through which a steady stream of air is bubbled. In a cell kept at 80 °C for 72 h, 1.21 mmol of CO_2 was observed by GC to have been produced while 2.71 mmol of electrons were passed through the cell. This corresponds to an average current efficiency of 90% for the conversion of CO and O_2 to CO_2 and electricity. During this time the $[Rh^I(CO)_2Br_2]^-$ electrocatalyst completed 15.1 cycles. The typical open circuit potential for this cell was ∼0.40 V. At the end of this run, $[AsPh_4]Cl$ was added to the anode compartment and $[Rh^I(CO)_2Br_2]^-$ was recovered quantitatively as a pale yellow solid, as confirmed by its characteristic IR spectrum.[20]

We have thus shown that $[Rh(CO)_2Br_2]^-$ is an electrocatalyst for the oxidation of CO to CO_2 and that fuel cells based on homogeneous electrocatalysts can be constructed. Homogeneous electrocatalysts offer the ability to function efficiently at relatively low temperatures and may find significant applications in fuel cell research.

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Registry No. CO, 630-08-0; $[Rh(CO)_2Br_2]^-$, 44516-32-7.

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[19] k^h is obtained at E_p = 0.66 V vs. SCE. RDE area: 0.0491 cm^2.

[20] IR (Nujol) ν(CO) 2060 (vs), 1980 (vs) cm^{-1}. See ref 11 and 14.

Photochemistry of Perfluoro-3-diazo-2-butanone[1]

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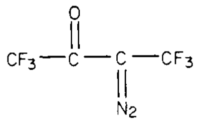
Stimulated by the hope of preparing the first observable oxirene,[3,4] we undertook several years ago an infrared study of the photolysis in matrix isolation of the title compound (**1**).[5] Our quest brought to light some interesting photochemistry but failed to yield detectable amounts of either perfluorodimethyloxirene (**2**) or a ketocarbene (**3**) intermediate. We were thus surprised by the recent report of Strausz et al.[6] that matrix photolysis of



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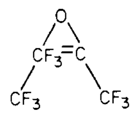

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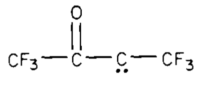

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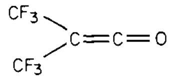

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[1] This report is based principally on the Ph.D. Dissertation of E.D.L. (Laganis, E. D. Ph. D. Dissertation, Dartmouth College, Hanover, NH, 1979).

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