kcal/M),[6] and CO on Ni (3.3–4.2 kcal/M)[12] by using other desorption techniques.

The selectivity and reactivity of molecular rearrangements on Pt surfaces have been found to be strongly dependent on the surface structure.[8] We have also observed this phenomenon: the Pt foil used in the above experiments was annealed to 800 °C before each measurement. Surfaces that were roughened by ion sputtering exhibited a different behavior. Details of the decomposition of both C_6F_6 and C_2F_4 on Pt surfaces are presently under investigation by DRS and Auger, X-ray, and UV electron spectroscopy.

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Electroreduction of CO to CH_4 and C_2H_4 at a Copper Electrode in Aqueous Solutions at Ambient Temperature and Pressure

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Carbon monoxide is a substance of primary importance from the viewpoint of utilization of carbon resources. Hydrogenation of CO in the gas phase has been widely studied, but only a small number of papers has been published about electrochemical reduction. Electroreduction of CO did not proceed effectively according to the previous papers;[1] the cathodic partial currents for electroreduction of CO were very small, not exceeding 5 × 10^{-5} A cm^{-2}. We briefly describe here an electroreduction of CO at a Cu cathode in aqueous solutions. This procedure allows an effective cathodic reduction of CO to form hydrocarbons and alcohols with appreciable current densities.

An electrodeposited copper sheet (purity 99.999%), donated by Sumitomo Metal Mining Co. Ltd., was cut into an electrode (20 × 20 × 1 mm) with a copper lead strip attached. We did not mount the electrode in resin in order to avoid possible contamination of the boundary interface of electrode/resin. The electrode was polished with fine emery paper (no. 1500), electrolytically polished in 85% phosphoric acid for ca. 2 min at ambient temperature, and then rinsed with doubly distilled deionized water. Electrochemical measurements were conducted at 18 °C with a three-compartment cell in which two anode compartments faced each side of the Cu electrode. The cathode compartment (36-mm inner diameter) was separated from the two anodes with sheets of cation exchange membrane (Selemion). The potential of the cathode was measured with respect to an Ag/AgCl reference electrode. The electrode potential was corrected for the IR drop between the Luggin capillary tip and the cathode. The catholyte (60 mL) was prepared from doubly distilled deionized water and reagent grade chemicals. The catholyte was purified by preelectrolysis with a 30 × 20 mm Pt black cathode at 2.5 × 10^{-5} A cm^{-2} under purified N_2 atmosphere for more than 15 h. The Pt black cathode was regenerated by anodic polarization in 0.5 mol dm^{-3} H_2SO_4 before use. Carbon monoxide (high purity grade, >99.95%, hydrocarbon content <0.5 ppm, dew point below −65 °C), purchased from Nihon Sanso Co. Ltd., was introduced to the catholyte after passing through a KOH solution.

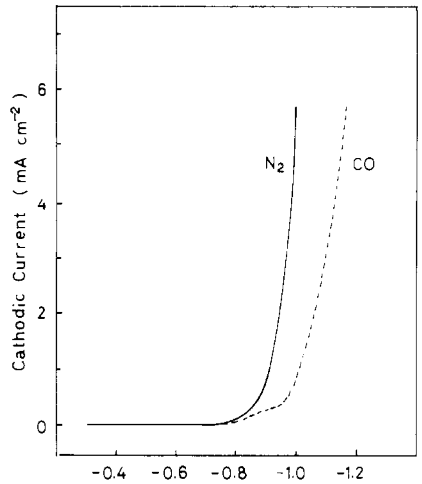

Figure 1. Voltammograms obtained in a phosphate buffer solution (0.17 M KH_2PO_4/0.03 M K_2HPO_4, pH 6.1) saturated with N_2 or CO. Scan rate 50 mV s^{-1}.

Voltammetric measurements were conducted with electrolytes saturated with purified CO or N_2. Coulometric measurements at constant currents were conducted in $KHCO_3$, KOH, and a phosphate buffer aqueous solution with CO bubbled into the catholyte (flow rate: ca. 70 mL min^{-1}) for 30 min; the catholyte was stirred vigorously with a magnetic stirrer.

CH_4 and C_2H_4 in the effluent gas from the cell were analyzed at 5-min intervals by a gas chromatograph equipped with an FID detector (Shimadzu 3BF). H_2 was analyzed by a gas chromatograph equipped with a TCD detector (Shimadzu 3AH). The volume of the gas sampling tube was 3 mL. The analytical data were averaged over 30 min of electrolysis. The limit of quantitative analysis was 0.6 ppm for CH_4 and 0.3 ppm for C_2H_4; these values correspond to a faradaic yield of 0.1% in a constant current (2.5 mA cm^{-2}) electrolysis. C_2H_5OH and n-C_3H_7OH in the solution were also analyzed after electrolysis by a gas chromatograph (Shimadzu 3BF). Formaldehyde in the solutions was determined by the chromotropic acid colorimetric method. The limit of quantitative analysis for the soluble products was 3 × 10^{-6} mol dm^{-3} for C_2H_5OH and n-C_3H_7OH and 0.1 × 10^{-6} mol dm^{-3} for HCHO. The faradaic yields for these limits are 0.3% for C_2H_5OH and n-C_3H_7OH and 0.002% for HCHO. The following analytical columns were employed for the identification of the products by the gas chromatograph; molecular sieve 5Å and 13X, Porapak N + Porapak Q, activated alumina TR, and silica gel for CH_4; Porapak N + Porapak Q, activated alumina TR, and silica gel for C_2H_4; Porapak Q, PEG 400/Chromosorb, Unisole 30T (alkylene glycol phthalate)/Chromosorb, and PEG 20M/Shimalite for C_2H_5OH; PEG 400/Chromosorb, Unisole 30T/Chromosorb, and PEG 20M/Shimalite for n-C_3H_7OH. The formation of CH_4 and C_2H_4 was also confirmed by a gas chromatograph mass spectrometer.

Figure 1 shows voltammograms obtained for N_2 and CO saturated phosphate buffer solutions (pH 6.1). The cathodic current is greatly suppressed in the presence of CO. Anodic oxidation of CH_3OH, as is well known, is markedly interfered with by some intermediate species formed in the reaction, e.g., by CO adsorbed on the electrode or some other related species.[2] Adsorption of

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(1) (a) Petrova, G. N.; Efimov, O. N.; Strelets, V. V. *Izv. Akad. Nauk SSSR. Ser. Khim.* **1982**, 2608–2610. (b) Uribe, F. A.; Sharp, P. R.; Bard, A. J. *J. Electroanal. Chem.* **1983**, *152*, 173–182. (c) Yoneyama, H.; Wakamoto, K.; Hatanaka, N.; Tamura, H. *Chem. Lett.* **1985**, 539–542. (d) Yamamura, S.; Kojima, H.; Kawai, W. *J. Electroanal. Chem.* **1985**, *186*, 309–312. (e) Ogura, K.; Takagi, M. *Ibid.* **1985**, *195*, 357–362. (f) Kolyagin, G. A.; Danilov, V. G.; Kornienko, V. L. *Elektrokhimiya* **1985**, *21*, 133–135.

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Table I. Faradaic Efficiencies of Various Products from the Electroreduction of CO at a Cu Electrode in Aqueous Solutions

electrolyte	pH	potential vs. SHE	faradaic efficiency/%						
			CH_4	C_2H_4	EtOH	*n*-PrOH	HCHO	H_2	total
				Current 1.0 mA cm^{-2}					
phosphate[a]	6.1	-1.10	0.3	1.7	0.0	0.0	0.2	91.4	93.6
$KHCO_3$[b]	9.4	-1.29	1.1	21.6	1.3	2.0	0.04	63.3	89.3
				Current 2.5 mA cm^{-2}					
phosphate[a]	6.1	-1.18	9.3	2.3	0.0	0.0	0.2	81.1	92.9
$KHCO_3$[b]	9.6	-1.40	16.3	21.2	10.9	1.5	0.1	45.5	95.5
				Current 5.0 mA cm^{-2}					
phosphate[a]	6.0	-1.21	16.8	1.7	0.0	0.0	0.02	75.4	93.9
$KHCO_3$[b]	9.6	-1.45	16.2	5.5	2.7	0.3	0.03	65.4	90.1
KOH[c]	12.9	-1.47	1.0	14.1	5.8	1.1	0.05	70.7	92.8

[a] Phosphate buffer solution containing KH_2PO_4 (0.17 mol dm^{-3}) and K_2HPO_4 (0.03 mol dm^{-3}). [b] $KHCO_3$ (0.1 mol dm^{-3}). [c] KOH (0.1 mol dm^{-3}).

CO or of other molecules may prevent the H_2 evolution in the present system as well. A small hump appears at -0.86 V vs. SHE in the voltammogram obtained for CO-saturated solution. A coulometric measurement at a controlled electrode potential of -0.86 V vs. SHE yielded only H_2, and the faradaic efficiency for H_2 formation was more than 97%. The source of the hump is not clarified yet at the present stage.

The gaseous products, CH_4, C_2H_4, and H_2, appeared in the effluent gas after the electrolysis started; the concentrations remained virtually constant during the electrolysis. C_2H_6 was not detected in the effluent gas. CH_4, C_2H_4, and H_2 were not detected in the effluent gas (CO) within the limit of detection before the electrolysis started. The products contained in the electrolytes were C_2H_5OH, n-C_3H_7OH, and HCHO. CH_3OH was not detected in the solution. These soluble products were not found within the limit of detection in a blank experiment carried out under exactly the same conditions without electrolysis. Table I presents the faradaic efficiencies of products obtained in various coulometric measurements. The faradaic efficiencies were calculated on the basis of the number of electrons required for the formation of one molecule of the products from CO and H_2O: six for CH_4, eight for C_2H_4, eight for C_2H_5OH, 12 for n-C_3H_7OH, two for HCHO, and two for H_2. The total values of the faradaic efficiency exceed 90%. Hence the tabulated substances are the major products of the reaction.

The partial current for CO reduction (I_c) exceeds 1 mA cm^{-2} for $KHCO_3$ solution at -1.40 V vs. SHE with the total electrolytic current of 2.5 mA cm^{-2}. The overvoltage of the reaction is large ($E°(CO/CH_4) = -0.31$ V, $E°(CO/C_2H_4) = -0.40$ V vs. SHE at pH 9.6).[3] However, the value I_c obtained in this study is much higher than any values reported in the previous papers, i.e., less than 5×10^{-5} mA cm^{-2}. This I_c appears to be of the same order of magnitude of the limiting current due to the transport of CO to the electrode, since the solubility of CO is low in water.

Table I shows some remarkable features of this reaction. The production of C_2H_4 prevails over that of CH_4 at less negative potentials (less total current) and at higher pH solutions. The increased formations of C_2H_5OH and n-C_3H_7OH are accompanied with high faradaic efficiencies of C_2H_4. Hence, C_2H_4, C_2H_5OH, and n-C_3H_7OH will be formed via some common intermediate species. H_2 formation is markedly interfered with CO or CO related species adsorbed on the electrode, as indicated in Figure 1. These adsorbed species will probably be reduced at more negative potentials to yield hydrocarbons and alcohols.

The Cu electrode, etched in 6% HNO_3 aqueous solution instead of by electropolishing, was also tested for the cathode. Electrolysis with this electrode was conducted with 0.1 M $KHCO_3$ at 2.5 mA cm^{-2}. The current efficiencies for the products were as follows: CH_4, 20.4%; C_2H_4, 8.3%; C_2H_5OH, 3.7%; n-C_3H_7OH, 0.14%; HCHO, 0.02%; H_2, 63.4%. These values are close but not exactly equal to those obtained with an electropolished electrode (Table I). The reason is unknown at present.

We previously reported the production of CH_4 and C_2H_4 in electrochemical reduction of CO_2 at a Cu electrode in aqueous $KHCO_3$ solution.[4] The present results suggest that the electroreduction of CO_2 may proceed with CO or CO-derived intermediates formed at the Cu electrode.

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[3] Estimated from thermodynamic data. *Lange's Handbook of Chemistry*, 12th ed.; Dean, J. A., Ed.; McGraw-Hill, New York, 1979.

[4] Hori, Y.; Kikuchi, K.; Murata, A.; Suzuki, S. *Chem. Lett.* **1986**, 897–898.

Platinacyclobutanes on the Route to Cyclopropanation

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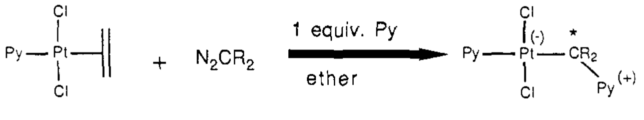
Recently we reported on the preparation and bonding character of platinum complexes arising from the reaction of platinum(II) with diazoderivatives (eq 1).[1] It was clear from these results that



(1)

R= H,H ; H,CH_3 and H, CO_2Et

Pt(II) cannot provide adequate orbital overlap with the electrophilic carbon * to form a π bond, and pyridine is required for stabilization. In this communication, results are reported on a similar reaction with use of diazofluorene which, in contrast to those cited above, can provide substantial stabilization of the electrophilic center by electron donation from the aryl moieties. These results not only impact on the mechanism of metal-facilitated cyclopropanations but also represent the first example of a platinum-catalyzed cyclopropanation. The results are shown in Scheme I.

To prepare **1e**, Zeise's dimer was reacted with 1 equiv of pyridine in chloroform yielding **1a** in quantitative yield. Subsequent reaction with diazofluorene in chloroform containing a second equivalent of pyridine gave the bright red complex **1e** in 94% yield. It was further purified by trituration with pentane and silica gel chromatography. From its ^{13}C, ^{1}H, and ^{195}Pt NMR spectra, structure **1e** was readily established. The data are as follows: ^{13}C ($CDCl_3$, ppm) -4.65 (t, $^{1}J_{Pt,C} = 376$ Hz, 2 C), 60.9 (s, $^{2}J_{Pt,C} = 95$ Hz, 1 C) and nine aromatic resonances at 153.4 (d, 2 C), 152.3 (s, 2 C), 149.3 (d, 4 C), 141.0 (s, 2 C), 138.1 (d, 2 C), 129.0 (d, 2 C), 125 (d, 4 C), 119.7 (d, 2 C), and 118.7 (d, 2 C) accounting for all 22 aromatic carbons. The resonances at

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