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Alcohol Electrooxidation Catalysts from Degraded Polyanionic Chelating Ligand Complexes. The Uncertainty for Catalyst Identification That Accompanies a Decomposing Catalytic System

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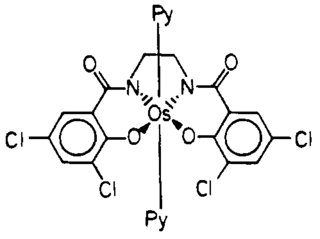
Electrooxidation of *trans*-Os(η^4-CHBA-Et)(py)$_2$, H_4CHBA-Et = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane, in the presence of alcohols led to the discovery of several catalytic systems for the electrooxidation of alcohols. The catalytic systems are formed via the oxidative and hydrolytic degradation of the ethylene unit of the polyanionic chelating (PAC) ligand [η^4-CHBA-Et]$^{4-}$ in a sequence that involves 15 observable species. The principal species in the catalytically active solutions have been identified. The uncertainty for catalyst identification that is inherent with decomposing catalyst systems is discussed. At high alcohol concentrations, primary alcohols are oxidized to aldehydes. Pure aldehydes are not oxidized. However, it has not been possible to study the catalytic oxidations at high concentrations of both primary alcohols and aldehydes. Cyclohexanol is oxidized to cyclohexanone. All the species in the degradation sequence are closely related. It is suggested that the principal species in the catalytic solutions might be able to carry out rapid inner-sphere oxidations of alcohols because of a higher affinity for alcohols than the noncatalysts in the degradation sequence.

Introduction

Catalyzed electrochemical oxidations of organic substrates such as alcohols[2] are receiving increased attention. In the process of developing new polyanionic chelating (PAC) ligands that are compatible with highly oxidizing metal centers,[3-9] we conducted controlled-potential electrolysis experiments on solutions of primary and secondary alcohols in the presence of trace quantities of *trans*-Os(η^4-CHBA-Et)(py)$_2$ (**5**) to search for alcohol electrooxidation catalysts. Electrocatalysts were indeed discovered, but early on in the work, it became obvious that the initial compound, **5**, was not a catalyst. We discovered that **5** undergoes a multistep ligand oxidation/hydrolysis sequence when electrooxidized in the presence of alcohols; the ethylene unit linking the two organic amide nitrogen atoms is degraded by sequential oxidation and hydrolysis events as shown in Scheme I.[3,10] It has been possible to show that the early species in the sequence are not catalysts. The catalytic systems eventually degrade to inactive material. We decided to study the degradation sequence and the catalytic reactions because this system provides an excellent illustration of the complexity that can be associated with a catalytic system that is undergoing degradation during the course of catalysis. In such circumstances, serious limitations can occur for catalyst identification (vide infra). The principal species in the catalytically active solutions have been identified. The characterizations of the compounds in the degradation sequence,[3] including detailed studies of the unusual isomerizations that result in the branching of the sequence into two parallel diastereomeric paths,[8] have been described previously.



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Experimental Section

All compounds were synthesized as previously described.[3] UV–visible spectra were recorded on a Hewlett-Packard 8450A diode array spectrophotometer.

Electrochemical Procedures. Dichloromethane (MCB or Mallinckrodt) used in electrochemical experiments was reagent grade and was further purified by passage over a column of activated alumina (Woelm N. Akt. I). TBAP (tetrabutylammonium perchlorate) supporting electrolyte (Southwestern Analytical Chemicals) was dried, recrystallized twice from acetone/ether, and then dried under vacuum. The TBAP concentration in all solutions was 0.1 M. Alcohols were reagent or spectrophotometric grade and were used as received.

Cyclic voltammetry was performed with a Princeton Applied Research Model 173 potentiostat equipped with positive-feedback *IR* compensation

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(1) Alfred P. Sloan Research Fellow, 1986–1988; Dreyfus Teacher-Scholar, 1986–1990.

(2) See, for example: (a) Shono, T. *Tetrahedron Lett.* **1979**, *20*, 3861–3864. (b) Shono, T.; Matsumura, Y.; Hayashi, J.; Mizoguchi, M. *Ibid.* **1979**, *20*, 165–168. (c) Shono, T.; Matsumura, Y.; Hayashi, J.; Mizoguchi, M. *Ibid.* **1980**, *21*, 1867–1870. (d) Leonard, J. E.; Scholl, P. C.; Steckel, T. P.; Lentsch, S. E.; Van De Mark, M. R. *Ibid.* **1980**, *21*, 4695–4698. (e) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310–2312. (f) Thompson, M. S.; DeGiovani, W. F.; Moyer, B. A.; Meyer, T. J. *J. Org. Chem.* **1984**, *25*, 4972–4977. (g) Meyer, T. J. *J. Electrochem. Soc.* **1984**, *131*, 221C–228C. (h) Yoshida, J. I.; Nakai, R.; Kawabata, N. *J. Org. Chem.* **1980**, *45*, 5269–5273. (i) Masui, M.; Ueshima, T.; Ozaki, S. *J. Chem. Soc., Chem. Commun.* **1983**, 479–480. (j) Semmelhack, M. F.; Chou, C. S.; Cortes, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 4492–4494. (k) Dvonch, W.; Mehltretter, C. L. *J. Am. Chem. Soc.* **1952**, *74*, 5522–5523. (l) Horowitz, H. H.; Horowitz, H. S.; Longo, J. M. In *Proceedings of the Symposium on Electrocatalysis*; O'Grady, W. E., Ross, P. N. J., Will, F. G., Eds.; The Electrochemical Society: Pennington, NJ, 1981; pp 285–288. (m) Baizer, M. M. *Organic Electrochemistry*; Marcel Dekker: New York, 1973; pp 821–838. For examples without catalysts, see: (n) Scholl, P. C.; Lentsch, S. E.; Van De Mark, M. R. *Tetrahedron* **1976**, *32*, 303–307. (o) Brown, D. R.; Chandra, S.; Harrison, J. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *38*, 185. (p) Mayeda, E. A.; Miller, L. L.; Wolf, J. F. *J. Am. Chem. Soc.* **1972**, *94*, 6812. (q) Horanyi, G.; Vertes, G.; Koning, P. *Naturwissenschaften* **1970**, *60*, 519–520.

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(10) Because of the complexity of the degradation sequence the compound numbering scheme is retained from prior work to assist with comparisons of papers.[3]

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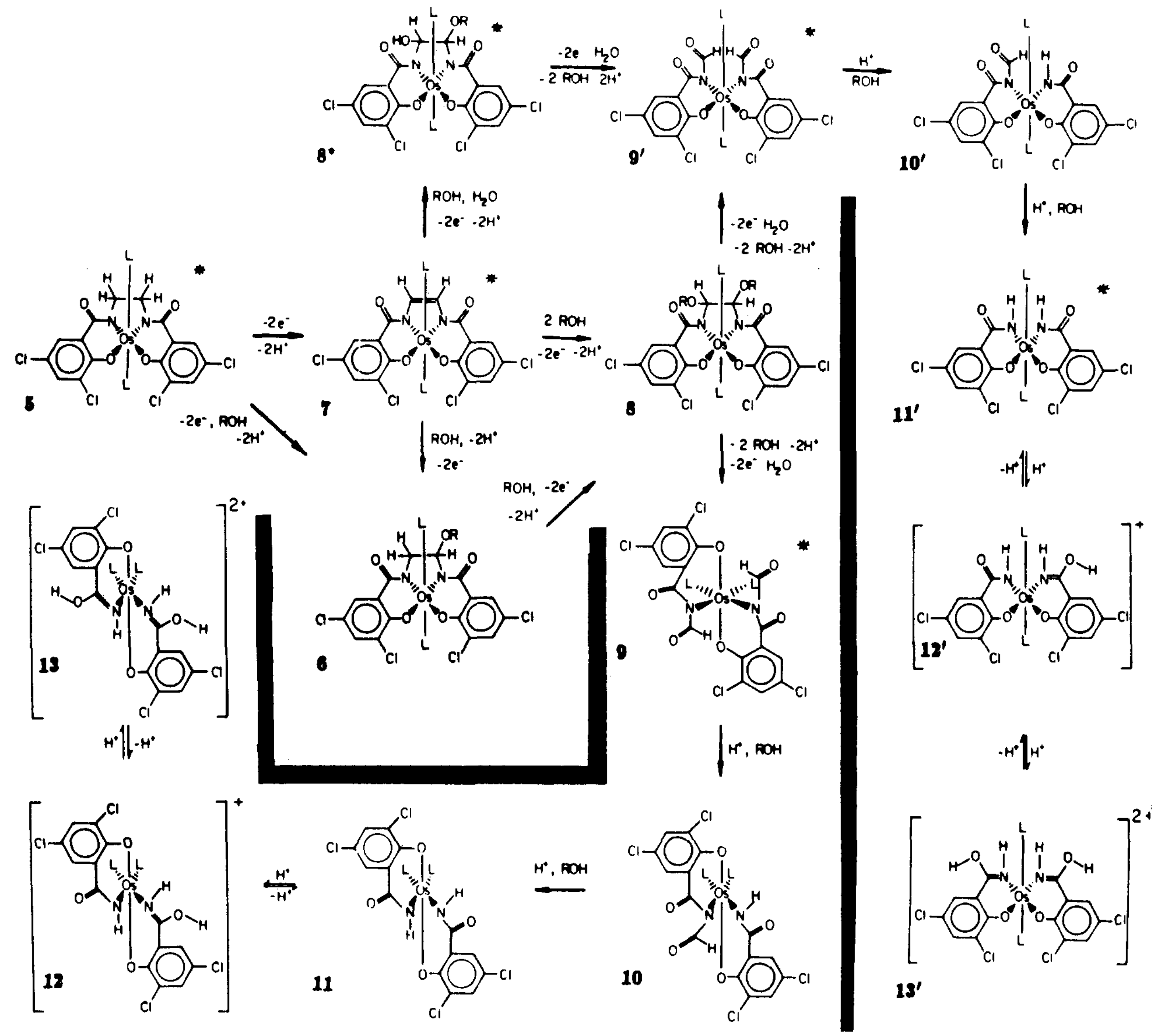
Scheme I[a]



[a] An asterisk denotes structures characterized by X-ray crystallography.

and a Model 175 universal programmer. Current–voltage curves were recorded on a Houston Instruments Model 2000 X-Y recorder. Standard two- and three-compartment electrochemical cells were used. When necessary, solutions were purged with argon to remove oxygen. The working electrode was a 0.17 cm^2 basal-plane pyrolytic graphite (BPG, Union Carbide Co.) disk mounted in a glass tube with heat-shrinkable tubing. The counter electrode was a platinum wire. Various reference electrodes were used including SCE, SSCE, Ag/AgCl, and a silver-wire quasi-reference electrode. For each compound studied at least one experiment was performed in the presence of ferrocene as internal potential standard. All potentials are quoted with respect to the formal potential of the ferrocenium/ferrocene couple, In CH_2Cl_2 under these conditions we have consistently measured this couple as +0.48 V vs. SCE. The formal potentials of all the couples were taken as the average of the anodic and cathodic peak potentials.

Controlled-potential electrolysis experiments were performed with the PAR Model 173 potentiostat equipped with a Model 179 digital coulometer using positive-feedback *IR* compensation. Electrolyses in dichloromethane were performed in a standard three-compartment H-cell with a platinum-gauze counter electrode in one compartment and the reference electrode and a 1.7 × 4.5 × 0.07 cm BPG working electrode in the third compartment. The reference electrode used for controlled-potential oxidations with the catalyst compounds was a Corning Ag/AgCl double-junction reference electrode. The product solutions containing decomposed catalysts were found to cause the potential of the usual single-junction Ag/AgCl reference electrode to drift by as much as 500 mV. Therefore, a double-junction reference electrode was used to maintain proximity of the reference electrode to the working electrode and minimize *IR* compensation but, at the same time, isolate the reference electrode from the catalyst solution. The inner compartment of the double-junction reference electrode contained an aqueous solution of saturated KCl and AgCl. The outer compartment contained this solution layered over CH_2Cl_2 containing 0.5 M TBAP. This arrangement gave potentials almost identical with those of the single-compartment electrode but was not susceptible to drift during the electrolyses. Most electrolyses were performed in the presence of Na_2CO_3, added to neutralize the acid formed by alcohol oxidation. All experiments were performed at room temperature, 22 ± 2 °C.

HPLC analyses for aldehydes and ketones were performed on an IBM LC 9533 ternary gradient LC equipped with an octadecyl column, an LC 9522 254-nm UV detector and a Hewlett-Packard 3390A integrator. The eluting solvent was 3:2 methanol/water (v/v). All analyses were performed immediately after the electrolyses to minimize the effects of air oxidation of the alcohols. The following procedure was used to prepare all samples. All of the anolyte solution was collected and filtered into a 100-mL flask. Benzoylhydrazine (50 mg) and trifluoroacetic acid (2 drops) were added and the solution was heated under reflux for 1 h. The CH_2Cl_2 was then removed on a rotary evaporator at 50 °C. The resulting oil was dissolved in methanol and diluted to 100 mL. The concentration of the product in the sample was determined by comparison of its HPLC peak area with that of the standard solution of the corresponding hydrazone of similar concentration. The hydrazone samples used for preparing the standard solutions were synthesized by reaction of benzoylhydrazine with the appropriate aldehyde or ketone in boiling ethyl acetate. The products were recrystallized several times from methanol and thoroughly dried. No residual benzoylhydrazine was visible upon TLC analysis. The analysis was tested on a sample of benzaldehyde (<100% pure) and returned 93% of the theoretical yield. Three standard solutions of benzaldehyde benzoylhydrazone spanning the concentration range obtained from the electrolyses gave a very linear plot of HPLC peak area vs. concentration with a zero intercept.

The current efficiency for production of the aldehyde or ketone product was calculated on the basis of a two-electron oxidation of the alcohol. The amount of carbonyl product formed was corrected for values obtained in blank experiments performed with the alcohols in the absence of catalyst. A correction was also applied for the charge consumed in the blank decomposition of the catalyst systems, approximately a three-electron process. The corrected values were then used to calculate the apparent current efficiency of the oxidation by using the formula

$$\mathrm{CE} = \frac{(N - N')(2F)}{Q - Q'} \times 100\%$$

where N = number of moles of product from electrolysis with catalyst, N' = number of moles of product from blank electrolysis, F = 96 485 C/mol, Q = charge passed during electrolysis with catalyst, and Q' = charge passed during blank electrolysis.

The maximum turnover number of the catalysts were determined from UV–vis data taken during the electrolyses. The electrolyses were stopped periodically, usually 4–7 times, to take spectra. If Na_2CO_3 was present, the solution was allowed to stand unstirred for several minutes. A sample was then taken and its spectrum measured. The sample was then returned to the electrochemical cell and the electrolysis was resumed. The electrolyses were generally ended when the absorbance had fallen to about 10%, since accurate measurements could not be made at lower absorbances, especially in the presence of Na_2CO_3. The absorbance of the visible band of the system at about 600 nm was then plotted as a function of the total charge passed at the time of the measurement. If Na_2CO_3 was present, the measured absorbance was corrected for scattering due to solid that had not completely settled. This was accomplished by subtracting the absorbance measured at 800 nm, where the catalysts did not absorb, from the absorbance of the 600-nm band. These plots gave linear sections that were extrapolated to zero absorbance to determine the maximum charge that could have been passed under the conditions of the experiment. This charge was then divided by the number of coulombs required for a one-electron oxidation of the osmium present to arrive at the reported maximum turnover number.

Results and Discussion

Electrocatalytic Oxidation of Alcohols. Possible Nature of the Catalysts. The sequence of ligand oxidation and hydrolysis reactions depicted in Scheme I ensues when complex **5** is electrooxidized at 0.97 V in the presence of alcohols (0.5–1.0 M). The initial current flow is associated with the oxidative degradation of the ethylene group forming a mixture of diastereomers **9** and/or **9′**. The conversions of **5** to **9** and/or **9′** require the passage of six electrons per mole of osmium. Over many experiments the experimental charge consumed is variable, but is always equal to or slightly greater than six electrons. When these compounds have been produced quantitatively there is a reduction in current flow.[3] The ratio of [**9**] and [**9′**] thus formed is dependent upon the conditions of the electrooxidation experiment such as the alcohol employed.[3] If the solution of **9** and/or **9′** is reexamined after a period of hours for catalytic activity, a large current flow is observed at 0.65 V that is associated with the catalytic electrooxidation of the alcohol present (vide infra). During the standing period the formimide ligands of **9** and/or **9′** undergo hydrolysis (or alcoholysis) to produce **11** and **11′**, respectively, which are then protonated by the acid generated from the PAC ligand oxidation.[3] Catalytically active solutions are produced rapidly if the solutions of **9** and/or **9′** are heated under reflux. The solutions contain equilibrium mixtures of **11** and/or **11′** and their mono and diprotonated forms **12** and **13** and/or **12′** and **13′**. It has been shown that the principal species present in the acidic solutions at the end of the ligand degradation sequence are **13** and/or **13′**.[3] These solutions show no tendency to undergo further changes upon prolonged standing.

The CV of **13** in dichloromethane containing 0.1 M TBAP shows only one reversible osmium(IV/III) couple at approximately +0.1 V (Fc^+/Fc). This CV remains unchanged upon addition of excess trifluoromethanesulfonic acid, indicating that the reversible couple is associated with the reduction of **13**. No waves associated with reduction of **11** or **12** are visible in the CV of **13** (Table I). In the absence of alcohol no anodic activity is seen below +1.1 V where oxidation of the medium by the electrode begins. Thus one-electron oxidation of dicationic **13** occurs at a potential equal to or more anodic than that at which medium oxidation is observed. Addition of benzyl alcohol to give a 1 M solution causes very large anodic currents at potentials above +0.65 V (Fc^+/Fc) (Figure 1). High concentrations of alcohol (greater than 0.1 M) are required to produce this anodic activity. No current flow was observed in the absence of **13**. Controlled-potential electrolyses have confirmed that this anodic activity is caused by the catalytic oxidation of benzyl alcohol to benzaldehyde. These experiments also reveal that the electrocatalysis has a finite lifetime (vide infra).

Table I. Electrochemical Data for Catalyst Precursor Compounds

	formal potential,[a] V		
compd	Os(III/II)	Os(IV/III)	cation/Os(IV)[b]
11-py	−1.90	−0.67	+0.71
11-*t*-Bupy	−1.99	−0.70	+0.72
11-*t*-Bupy	−1.97	−0.70	+0.63
17	[c]	−0.91	+0.54
15	[c]	−0.95	+0.52

[a] Measured in CH_2Cl_2 containing 0.1 M TBAP and referenced to Fc^+/Fc internal standard. [b] Peak potentials for nonreversible oxidation to osmium(V). [c] Not measured.

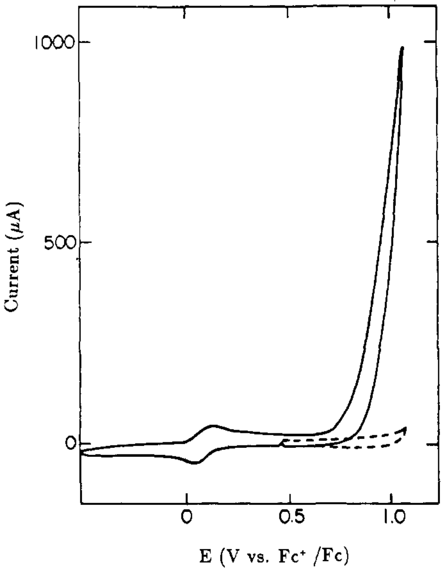


Figure 1. (—) Cyclic voltammogram of 1 mM **13** + 1 M benzyl alcohol in CH_2Cl_2 containing 0.1 M TBAP at 0.17 cm^2 BPG electrode. Scan rate = 200 mV/s. (- -) Response with alcohol or catalyst alone.

Most of the complexes in Scheme I have been isolated as pure crystalline materials. When the pure materials are added to fresh dichloromethane solutions containing high concentrations of alcohol, with and without added acid, compounds **5**, **7**, **8**, **8***, **9**, and **9′** do not show the large anodic activity found with **13**, although a smaller current flow is observed with the first four species that can be attributed primarily to the progress of the ligand degradation sequence.[3] Indirect evidence suggests that the TLC-detectable complex of probable structure **6**[3] is not a catalyst. No surge in current flow is observed while the sequence is passing through this intermediate. Similar findings were made for complexes **10** and **10′**.[3] Catalysis appears to be limited to those solutions containing the mono- and diprotonated forms of **11** and **11′**.

Several pieces of circumstantial evidence indicate that the nonprotonated compounds, **11** and **11′**, are not catalytically active. Figure 2 shows a cyclic voltammogram of **11** in the presence of 1 M benzyl alcohol. The initial cathodic scan shows the osmium(IV/III) couple of **11** at E_f = −0.67 V. A shoulder, visible in the first anodic scan, corresponds to nonreversible oxidation of the osmium(IV) species, **11** (Table I). However, on the return scan, after some catalytic oxidation has proceeded, the reduction wave for the osmium(IV/III) couple of **13** appears. The shoulder

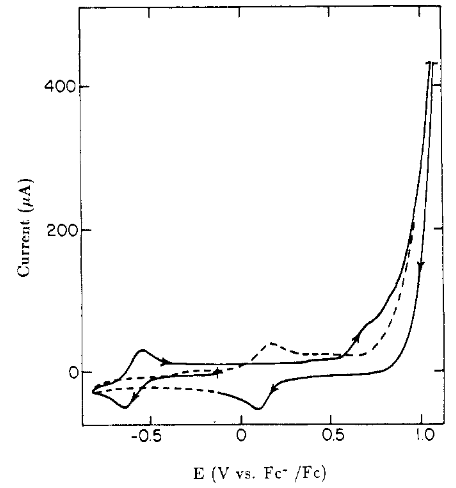
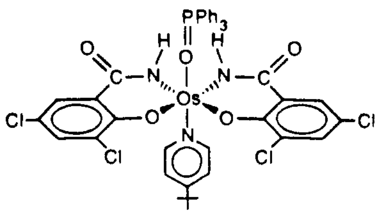


Figure 2. (—) Cyclic voltammogram of 1 mM **11** + 1 M benzyl alcohol in CH_2Cl_2 containing 0.1 M TBAP at 0.17 cm^2 BPG electrode. Scan rate = 200 mV/s. (- -) Second scan.

attributed to the oxidation of **11** is not visible in the second and succeeding scans (Figure 2). Apparently the acid formed by the alcohol oxidation (2 equiv/mol of alcohol oxidized) protonates **11** in the immediate vicinity of the electrode (cyclic voltammetry experiments are conducted without stirring), so that on the second and subsequent scans the osmium(IV/III) couple of **13** at +0.1 V is observed. The appearance of the shoulder in Figure 2 is significant. It suggests that oxidation of **11** is a separate event from the catalytic reaction, i.e. that **11** is not a catalyst. The triphenylphosphine oxide containing compounds **15** and **17** (**15** is a cis isomer of **17**)[3] also give catalytically active solutions. These species are nonreversibly oxidized to monocations at lower potentials than **11** (see Table I), and the waves for oxidation of the nonprotonated forms are clearly separated from the catalytic waves. Therefore, it is highly unlikely that the nonprotonated forms are catalysts. Returning to Figure 2, one might consider that since compounds **11**–**13** are in equilibrium, trace quantities of **12** and **13** could be present in the protic medium to initiate the catalysis. The catalytic oxidation generates acid to convert the osmium complexes to their diprotonated forms. Thus, the experiment depicted in Figure 2 suggests that **12** and **13** might be catalytically active.



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As noted above, in the absence of alcohol the CV of **13** in dichloromethane shows no oxidation process. Thus, oxidation of **13** occurs at a potential more positive than +1.1 V (where the medium employed for these experiments is oxidized). Since the electrooxidation process begins at +0.65 V, any catalysis process based on **13** would have to shift the potential for oxidation of **13** very significantly. Alcohol or alkoxide coordination might effect such a shift. CV results indicate a decrease in the currents for benzyl alcohol oxidation (i.e. decreased catalytic rate) upon addition of excess trifluoromethanesulfonic acid (vide infra). Electrolysis experiments also showed decreased currents as the concentration of acid increased. As the acid concentration is increased, the concentration of **12** should be decreased in favor of **13**. If **13** is inactive or less active than **12**, reduced catalytic currents would be observed. This is another piece of indirect evidence that might be considered an indication that the more likely catalyst is **12** and not **13**. However, it should be noted that an alcohol complex of **12** and an alkoxide complex of **13** are tautomers. It is therefore unrealistic at this point to treat **12** and **13** as separate species when considering their possible relative roles in the catalytic electrooxidations. The equilibria shown in Scheme II are consistent with the results we have described. If alcohol coordination is a necessary component of alcohol oxidation, the rate suppression effected by added acid might be caused by inhibition of alcohol coordination to either **12** or **13**.

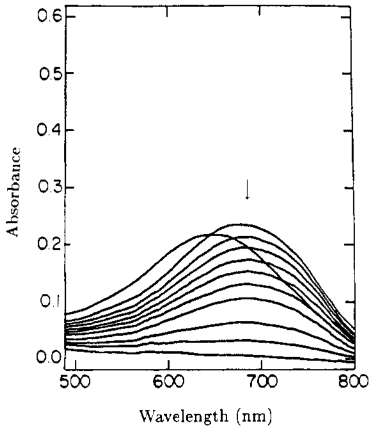

Figure 3. UV–vis spectra taken during controlled-potential electrolysis of 60 μM **13** + 0.5 M benzyl alcohol in CH_2Cl_2, 0.1 M TBAP at +0.97 V.

Scheme II

$$\mathbf{13} + ROH \rightleftharpoons [\mathbf{13}(OR)]^- + H^+ \rightleftharpoons [\mathbf{12}(HOR)]^- + H^+$$

$$ROH + H^+ \rightleftharpoons [ROH_2]^+$$

Unfortunately, the catalyst species produced in this work are finite-lived. In the following section we describe how catalyst lifetimes were determined and then proceed with an analysis of the effects of reaction conditions on the catalytic reactions.

Procedure for Determining Catalyst Lifetime. Controlled-potential electrolyses were performed to verify that the observed anodic activities arose from the oxidation of alcohols to aldehydes and ketones. A solution containing the osmium complex (ca. 50 μM) and the alcohol (usually 0.5 M) was oxidized at a basal-plane pyrolytic graphite (BPG) working electrode at a potential where anodic activity was observed (usually +0.97 V). The concentrations of the carbonyl compounds were determined by HPLC analysis (after derivatization with benzoylhydrazine). Control experiments were performed with the alcohols in the absence of catalyst to verify that no significant amount of uncatalyzed oxidation took place and to provide blank charge and carbonyl product concentration data for use in calculating the current efficiency of the catalytic oxidations. The charge consumed in the further decomposition of the osmium complexes to inactive solutions was determined by controlled-potential electrolyses of solutions of the compounds listed in Table I. In each case, very close to 3 faraday/mol of osmium was consumed. This correction has been applied to all current efficiency (CE) calculations.

During the electrolysis experiments the current steadily decreased as the color of the blue color faded, until a steady low current and a colorless or pale yellow solution resulted. A series of UV–vis spectra obtained during an electrolysis of benzyl alcohol with added **13** is shown in Figure 3. The absorbance initially increased slightly with the generation of acid as the equilibria **11** $\rightleftharpoons$ **12** $\rightleftharpoons$ **13** adjusted and the position of the visible band shifted to a region characteristic of **13**. The absorbance of this band then decreased in a regular manner. A plot of absorbance of this band as a function of charge passed during the electrolysis is linear (Figure 4), except for the initial period, during which the absorbance increases slightly as the concentration of **13** increases. Similar plots were obtained with **11′**, **11**-*t*-Bupy, **15**, and **17**.

These linear plots of absorbance versus charge passed were very useful, since they allowed a simple, accurate assessment of the effects of changing reaction conditions on the lifetimes, or maximum turnover numbers, of the catalysts. It was very difficult

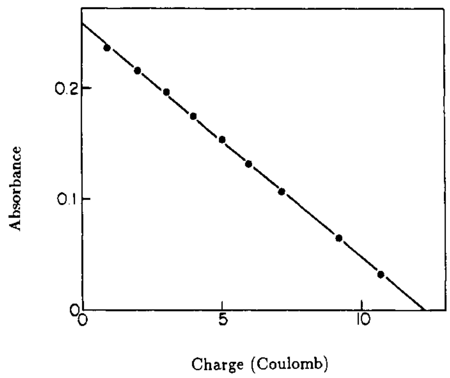

Figure 4. Plot of absorbance vs. charge with data taken from Figure 3 for electrolysis of 60 μM **13** + 0.5 M benzyl alcohol.

Table II. Effects of Reaction Conditions on the Oxidation of Benzyl Alcohol with Added **11**[a]

[**11**], μM	[BzOH], M	E,[b] V	base	CE,[c] %	max TN[d]
48	0.5	+0.97	none	99	247
37	0.5	+0.97	py		224
55[e]	0.5	+0.97	Na_2CO_3	94	205
23	0.5	+0.97	Na_2CO_3	98	254
224	0.5	+0.97	Na_2CO_3	99	91
64	0.5	+1.07	Na_2CO_3	high	159
56	0.5	+0.87	Na_2CO_3	high	136
56	0.1	+0.97	Na_2CO_3	high	40
52	1.0	+0.97	Na_2CO_3	high	297

[a] Electrolyses in CH_2Cl_2 containing 0.1 M TBAP at BPG anode. [b] Potential referenced to Fc^+/Fc. [c] Current efficiency for production of benzaldehyde determined by HPLC analysis and corrected for blank experiment in absence of catalyst. "High" CE indicates no blank was run. [d] Maximum turnover number determined by extrapolation of absorbance vs. charge plots to zero absorbance. [e] Average of six separate experiments.

to estimate the point at which all the catalyst had decomposed, because the catalytic current decreased very slowly near the end and never reached the true background level. However, by extrapolating the absorbance vs. charge-passed plots to zero absorbance, the maximum charge that could have been passed was estimated. This method was more accurate and time efficient than the direct measurement. The charge determined by extrapolation and the known amount of catalyst were then used to calculate the maximum turnover number (that we have chosen to express as a one-electron turnover number) for a given catalyst under a particular set of experimental conditions.

Effects of Reaction Conditions upon Catalytic Processes. The effect of changes in reaction conditions on the lifetime of the catalyst systems was investigated for the oxidation of benzyl alcohol with added catalyst precursor **11**. The results of this series of experiments are presented in Table II.

Under all conditions the benzyl alcohol is oxidized to benzaldehyde with high current efficiency. However, the lifetime of the **11** $\rightleftharpoons$ **12** $\rightleftharpoons$ **13** system and the maximum turnover number are significantly affected by the reaction conditions. As noted above, CV and bulk electrolysis experiments indicate a decrease in the currents for benzyl alcohol oxidation (i.e. decreased catalytic rate) with the addition of excess trifluoromethanesulfonic acid.

One way to prevent buildup of acid during the electrolyses was to add a base such as pyridine periodically to neutralize the acid being formed. This experiment had to be performed with less than a stoichiometric equivalent of pyridine, since the oxidized osmium complexes reacted in an unknown manner with excess pyridine. Upon addition of base the catalyst lifetime was only marginally affected, but the reaction did not slow down significantly in the latter stages. Sodium carbonate was a very effective base for this purpose, offering the advantages of high purity, selective reactivity with excess acid, simple removal at the end of the experiment by filtration, and no interference with the product analyses. A small decrease in lifetime was observed with sodium carbonate, but current efficiencies were still high and reaction times were lowered as with pyridine.

Table III. Oxidation of Benzyl Alcohol with Different Catalyst Species[a]

catalyst precursor	[catalyst], μM	CE,[b] %	max TN[c]
11	55	94	205
11-*t*-Bupy	56	100	216
11-*t*-Bupy	52	100	36
17	48	100	147
15	52	100	132

[a] Electrolyses conducted in CH_2Cl_2 containing 0.1 M TBAP at BPG anode at 0.97 V with excess Na_2CO_3 present. [BzOH] = 0.5 M. [b] Current efficiency for production of benzaldehyde determined by HPLC analysis and corrected for blank experiment run in absence of catalyst. [c] Maximum turnover number determined by extrapolation of absorbance vs. charge plots to zero absorbance.

The third entry in Table II represents an average of six experiments. In one experiment, the solution was purged with argon during the electrolysis, and in another, tetrabutyl ammonium tetrafluoroborate was substituted for TBAP as supporting electrolyte. Neither change had any significant effect on the results of the electrolyses. Thus, oxygen and anions of the supporting electrolyes are probably not important in the catalyst decomposition. This series of experiments allowed an estimation of the reproducibility of the electrolysis experiments. For these six experiments the average maximum turnover number was 205 with a standard deviation of 18%. The average current efficiency was 95% with a standard deviation of 3.6%.

The concentrations of osmium and alcohol have an effect on the catalyst turnover number. At lower alcohol/osmium concentrations the lifetimes are shorter. This implies that alcohol oxidation and catalyst decomposition compete, with catalytic alcohol oxidation competing more effectively at higher alcohol/osmium concentrations.

The dependence of the lifetime on the potential at which the experiment is performed is complicated. The most convenient potential for conducting the electrolyses was +0.97 V (vs. Fc^+/Fc, +1.5 V vs. Ag/AgCl reference electrode used to control the potential). At this potential significant catalytic activity was observed, but no uncatalyzed alcohol oxidation occurred. This also appears to be the optimum operating potential for the system, since at both higher and lower potentials the lifetime dropped significantly.

On the basis of the results in Table II a standard set of conditions was chosen for further studies with other catalyst compounds and other alcohols. These conditions were 50–60 μM catalyst precursor, 0.5 M alcohol, and +0.97 V, with sodium carbonate present to remove excess acid. The oxidation of benzyl alcohol under these conditions was used to compare the current efficiencies and lifetimes of the different catalyst compounds. The results of this series of experiments are listed in Table III.

Several points from Table III are noteworthy. The small change in the catalyst system associated with replacement of pyridine with 4-*tert*-butylpyridine in compound **11** has no significant effect on the catalyst lifetime. However, the **11**-*t*-Bupy system has a larger maximum turnover number (216) than the analogous trans system **11**-*t*-Bupy (36). *trans*-**17** and *cis*-**15**[3b] have similar, but intermediate maximum turnover numbers. These figures suggest that the differences in the rate of catalysis vs. the rate of decomposition induced by these monodentate ligand changes are small.

In Table IV a further set of experiments is presented where oxidations of alcohols other than benzyl alcohol have been studied employing the **11** system under the standard set of conditions. This information shows that benzyl alcohol is by far the best substrate of the alcohols tested for this system. Cyclohexanone was produced from cyclohexanol and *n*-heptanal was produced from *n*-heptanol, but the maximum turnover numbers were much smaller than with benzyl alcohol.

Conclusion

It is a well-established principle that simply showing that a species is the only detectable entity in a catalytically active solution

Table IV. Oxidation of Alcohols with the **11** System[a]

alcohol	[**11**], μM	CE,[b] %	max TN[c]
benzyl	55	94	205
cyclohexyl	56	97	10
n-heptyl	56	89	14
trans-2-hexenyl	56	d	8
allyl	56	d	6
none	60		3

[a] Electrolyses conducted in CH_2Cl_2 containing 0.1 M TBAP at BPG anode at +0.97 V with Na_2CO_3 present. [alcohol] = 0.5 M. [b] Current efficiency for production of aldehyde or ketone determined by HPLC analysis and corrected for blank experiment run in absence of catalyst. Current efficiencies are effectively quantitative when correction for charge consumed in catalyst degradation is applied. [c] Maximum turnover number determined by extrapolation of absorbance vs. charge plots to zero absorbance. [d] Not determined. HPLC analysis not applicable because of large blank values. Some allylic alcohols are known to be oxidized by (*p*-nitrophenyl)hydrazine.[11]

is far from sufficient evidence for considering that species to be the actual catalyst. Further evidence, such as a demonstration of kinetic competency, is required. This study illustrates an additional uncertainty that is associated with a catalytic system that undergoes degradation during the course of catalysis. Suppose in a catalysis study it can be demonstrated that the loss of catalytic activity coincides with the disappearance of some known complex which degrades to inactive material. In the absence of a study of the degradation process this information is of limited value as evidence that either the complex in question or some entity related to it by nondegradation processes is a possible catalyst. The actual catalyst could be a short-lived degradation intermediate. If the first degradation step is rate-determining, loss of catalytic activity will coincide with disappearance of the starting compound. If the intermediates in the degradation process have been characterized and it can be shown that the system is active only while one intermediate is present, much more can be inferred about the nature of the catalyst.

In the present study, the rates and sequential nature of the degradation processes allow many of the intermediates in the degradation sequence to be observed.[3] The slowest steps are associated with hydrolysis of the imido ligands of compounds **9** and **10**. All the compounds of Scheme I are dark blue species with the exception of the yellow **7**. The majority of the degradation intermediates can be shown to be catalytically inactive. When the degradation sequence is allowed to proceed uninterupted from **5** through the catalytically active solution to the inactive solution, the only visible change accompanying the loss of catalytic activity is a gradual fading of the dark blue solution to give a pale yellow solution. Direct or circumstantial evidence has been presented to indicate that complexes **12** and **12′** and/or **13** and **13′** in Scheme I could be catalysts. However, because these species occur at the end of the portion of the degradation sequence that we were able to characterize, the uncertainty about whether catalysis occurs at these steps of the degradation sequence is reduced only by the knowledge that it does not occur before they are reached. The catalysts could easily be subsequent unidentified species in a continued degradation sequence.

There are a number of reports of electrocatalytic oxidation of alcohols.[2] The selective oxidation of secondary alcohols to ketones is usually straightforward, but the selective oxidation of primary alcohols to aldehydes is challenging for simple aliphatic alcohols. The oxidation of primary alcohols initially produces aldehydes, which are usually further oxidized to carboxylic acids or esters. The catalysts reported here catalyze the oxidation of primary alcohols to aldehydes without any detectable oxidation of the aldehydes to the acids. Many control experiments have demonstrated that aldehydes are not substrates for the catalysts in the absence of alcohols or water. However, with the possible exception of benzylic alcohols (where selective oxidation to aromatic aldehydes is commonly observed), it cannot be claimed that these are general catalysts for the selective transformation of primary alcohols to aldehydes. The oxidation of aldehydes by classical transition-metal oxidants may well proceed via the prior formation of the hydrates or hemiacetals.[12] These reactions are usually carried out in water. Aliphatic aldehydes, which are hydrated to a considerable extent, react at rates comparable to those of the alcohols.[12] However, benzaldehyde, which hydrates to a lesser degree, is 85 times less reactive than benzyl alcohol.[12] The lifetimes of the catalysts reported in this work are such that appreciable concentrations of aldehydes have not been produced. Control experiments, in which a 1:1 mixture of primary alcohol and its aldehyde are catalytically oxidized, were not informative because of the high concentrations of substrates needed to observe reasonable turnover numbers coupled with the limited sensitivity of our analytical techniques. It has not been possible to work meaningfully in mixed alcohol/aldehyde concentration regimes where aldehyde oxidation to acid would be detected with conventional oxidizing agents.

It is interesting to consider why only compounds **12**, **12′**, **13** and **13′** in Scheme I might be catalysts. The 15 compounds in Scheme I are closely related 16-electron osmium(IV) species that mostly exhibit similar formal potentials[11] for the reversible redox couples. Each can have an available site for coordination of an alcohol, and the Lewis acidity should increase upon one-electron oxidation. A number of the complexes in Scheme I appear to be sterically indistinguishable from **12** and **12′**, so steric effects are probably unimportant. If the assumption is made that **12** or **13** and the other protonated species are the catalysts, then the catalytic properties could be related to the positive charge of these compounds. The positive charge could make the protonated species better Lewis acids and, consequently, better inner sphere oxidants than the neutral compounds in the degradation sequence. If it assumed that this explanation is correct, then the point could be of value in designing new oxidizing agents. It may be possible to control the chemoselectivity of designed chemical oxidants by determining through coordination sphere design whether the reagent will perform inner- or outer-sphere oxidations.

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