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(11) Gas samples were analyzed using a Hewlett-Packard 5830A gas chromatograph containing dual 6-ft, 1/8-in.-diameter, Poropax Q (50–80 mesh) columns.
(12) In addition to the gaseous hydrocarbon products, small quantities, corresponding to 4% conversion of the Ru$_3$(CO)$_{12}$ carbonyl ligands, of methanol and ethanol (in the molar ratio 2.5:1) were detected in the solution obtained on acidification.
(13) When d^8 tetrahydrofuran was used with AlH$_3$, no deuterium incorporation was found in the resulting alkane products, confirming that these are not formed from decomposition of the solvent.
(14) Ethane is the other gaseous product formed; no (<0.001 mmol) methane, propane, or propene were detected.
(15) Small quantities of methanol and ethanol, corresponding to 4, 6, and 2% conversion of the carbonyl ligands for Cr, Mo, and W, respectively, were detected in the solution obtained on acidification.
(16) GLC–mass spectrometric analysis of the reaction mixture indicated the absence of products additional to those reported.
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Ligand Substitution Kinetics on Ethylenediaminetetraacetato Complexes of Ruthenium(II) and Ruthenium(III) Covalently Attached to Graphite Surfaces

Sir:

The recent successful attachment of a variety of transition metal complexes to electrode surfaces[1-21] is an important first step in their exploitation as electrocatalysts. Since catalytic reactions exhibited by transition metal complexes in homogeneous solution frequently commence with coordination of substrates to the metal center,[22] it is of interest to examine ligand substitution kinetics at metal complexes bound to electrode surfaces. A few preliminary reports have addressed this topic,[2,5,14,20,21] but data that would allow a direct quantitative comparison of the substitution kinetics at a complex in both attached and unattached states have not previously been available. In recent studies[20] we have given procedures for attaching the ethylenediaminetetraacetato complexes of ruthenium(II) and -(III) to graphite electrodes and in this report substitution kinetics with the attached complexes are described. Matsubara and Creutz[23] have very recently reported homogeneous substitution kinetics for the same complexes so that the effects of covalent attachment on the coordination kinetics can be discerned. The attachment produces a substantial decrease in the rate of ligand substitution on the Ru(III) complex and a possible source of this effect is suggested.

Procedures for pretreating and mounting the pyrolytic graphite electrodes have been given previously[14] as has one method for attaching 4-methylaminopyridine to the graphite surface by means of an amide bond.[14] In the present study, this ligand was attached to electrode surfaces containing carboxyl
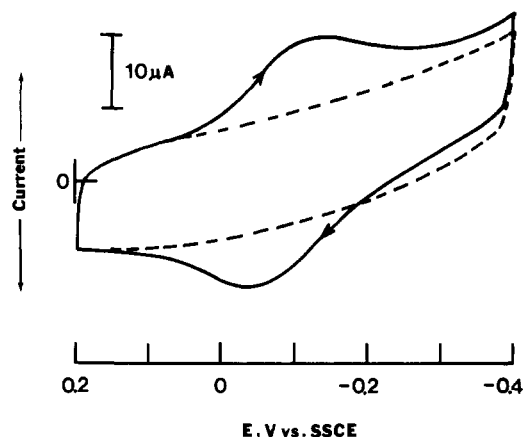

Figure 1. Steady-state cyclic voltammogram for Ru(edta) attached to a graphite electrode with the edge planes of the graphite exposed to the solution. An electrode that had been treated to produce –CONHCH$_2$-4-C$_5$H$_4$N groups on its surface was exposed to a 5 mM solution of Ru^{III}(edta)OH$_2$ for 4 h to produce the attachment. Dashed line: before exposure to Ru^{III}(edta)OH$_2$. Solid line: after exposure to Ru^{III}(edta)OH$_2$. Supporting electrolyte: 0.2 M CF$_3$COONa–0.03 M CF$_3$COOH (pH 1.5). Scan rate: 200 mV s^{-1}.
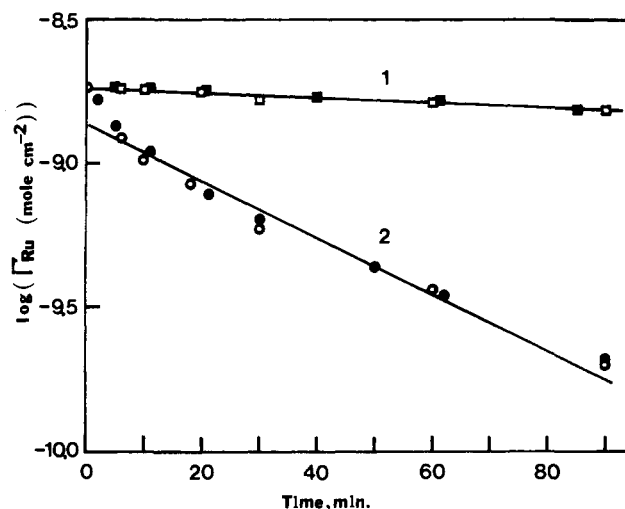

Figure 2. Time dependence of the quantity of Ru(edta) on graphite electrodes. 1: electrode potential maintained at −0.4 V; ruthenium oxidation state, +2; supporting electrolyte pH, 1.5 (■) and 6.4 (□). 2: electrode potential maintained at +0.2 V; ruthenium oxidation state, +3; supporting electrolyte pH, 1.5 (●) and 6.4 (○).

groups, introduced by plasma etching in oxygen,[19] by treating the electrodes and the ligand with dicyclohexylcarbodiimide in dichloromethane.[19] Following the attachment treatment the electrodes were washed with dichloromethane and methanol and dried under vacuum. The electrochemical cell, graphite electrode holder, and instrumentation for recording cyclic voltammograms have been described.[14] Potentials were measured with respect to a sodium chloride saturated calomel electrode (SSCE).

Aquoethylenediaminetetraacetatoruthenium(III) was prepared according to the procedure of Mukaida et al.[24]

Figure 1 shows a cyclic voltammogram for a pyrolytic graphite electrode to which Ru^{III}(edta) was bound by coordination to previously attached 4-methylaminopyridine ligands. (No response is obtained at electrodes that have not had the ligand attached to their surfaces.) The peak currents and areas of the cyclic voltammograms decreased slowly as the coated electrode was examined periodically in a 0.2 M sodium trifluoroacetate solution at pH 6.4 or 1.5 (trifluoroacetic acid). The rate of loss of the complex from the surface was greater when the electrode was maintained at a potential where the

ruthenium was in the +3 rather than the +2 oxidation state. In either oxidation state, the loss of the complex approximates first-order kinetics as shown in Figure 2. (The initially greater rate of loss of the Ru(III) complex may reflect the presence of some more highly reactive sites of attachment.) The departure of the complex from the surface results primarily from the breaking of the ruthenium–pyridine bond rather than the amide bond holding the ligand on the electrode surface because re-exposing a depleted electrode to a 5 mM solution of $Ru^{III}(edta)OH_2$ for 4 h resulted in replenishment of the attached complex to within 75% of its original value.

The rate constants obtained from the slopes of the lines in Figure 2 are 2×10^{-5} and 4×10^{-4} s^{-1} for the Ru(II) and Ru(III) complexes, respectively. These constants are to be contrasted with the values reported by Matsubara and Creutz[23] for the breaking of the ruthenium–heterocyclic nitrogen bond in the homogeneous complex of Ru(edta) with isonicotinamide.[25] These values are 3.5×10^{-6} [26] and 0.7 s^{-1} for the Ru(II) and Ru(III) complexes, respectively. There is thus a marked inhibition in the net rate at which the bond between the heterocyclic nitrogen atom and the Ru(III) center is broken when the complex is bound to the electrode surface. A small rate enhancement is observed with the attached $Ru^{II}(edta)$ complex.

A similar decrease in ligand substitution rates was observed (but not emphasized) in a previous report[20] where Ru(edta) was attached to graphite electrodes by amide bonds formed by condensation of the uncoordinated acetate group in Ru(edta) with amine groups that were introduced on the graphite surface by a plasma etching procedure.[19] In this case, the water molecule occupying a coordination position on the attached complex could be readily replaced with isonicotinamide (and similar ligands) when the ruthenium was maintained as Ru(II) but not if it was oxidized to Ru(III). This is opposite to the behavior of the unattached complexes where the Ru(III) form exhibits the greater reactivity toward ligand coordination.[23] The source of the reversal in relative reactivity produced by the attachment is not difficult to identify in this case: The remarkably high substitutional reactivity of the unattached $Ru^{III}(edta)$ complex[23] has been attributed[23] to labilization of the metal–water bond by intervention of the uncoordinated acetate group, an effect that is also observed with $Cr^{III}(edta)$[27] and $Co^{III}(edta)$.[28] When the uncoordinated acetate group is used to form an amide bond between the electrode surface and the complex, it is no longer available for labilization of the water–metal bond; so a decrease in substitutional reactivity is to be expected. Indeed, the difference in reactivity between the attached and unattached $Ru^{III}(edta)$ complex is evidence that an amide bond to the surface was formed by the attachment procedures.

In the present study the $Ru^{III}(edta)$ complex was attached by coordination of a bound ligand directly to the Ru(III) center so that the attached complex still contains an uncoordinated acetate group. That a significant decrease in reactivity is nevertheless observed suggests that the labilizing capacity of the acetate group is lessened considerably when the complex is attached to the surface. Supporting this interpretation is the fact that the same kinetics are observed in both neutral and acidic electrolytes (Figure 2). At pH 1.5 the uncoordinated acetate group in $Ru^{III}(edta)$ is protonated and the rates of the homogeneous substitution reactions of the complex are decreased markedly.[23] The lack of a corresponding pH sensitivity of the attached complex is good evidence that the acetate group is no longer an effective labilizing agent when the complex is attached.

The array of acetate groups carried by bound complexes might be expected to resemble the fixed groups in ion-exchange resins in that counterions will be closely associated with them. The formation of such ion pairs at the surface could pose a

substantial impediment to the labilizing action of the acetate groups and may be the origin of the decrease in substitutional reactivity of the bound complex.

The particular chemistry responsible for the unusual substitutional lability of $Ru^{III}(edta)$ complexes,[23] depending, as it does, on the intramolecular intervention of an uncoordinated, charge-bearing ligand, may be especially susceptible to modification by attachment to the electrode. The much smaller difference in reactivity between the attached and unattached $Ru^{II}(edta)$ complex (which does *not* exhibit a much greater reactivity than the corresponding ammine complex[23]) supports this idea. Experiments are underway in these laboratories with a variety of attached complexes in order to determine whether substitutional deactivation is the exception or the rule when coordination compounds are bound to electrode surfaces.

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Transfer of O_2 from a 4a-Hydroperoxyflavin Anion to a Phenolate Ion. A Flavin-Catalyzed Dioxygenation Reaction

Sir:

4a-Hydroperoxyflavin is believed to be an intermediate in the reactions catalyzed by two types of flavoenzyme mo-