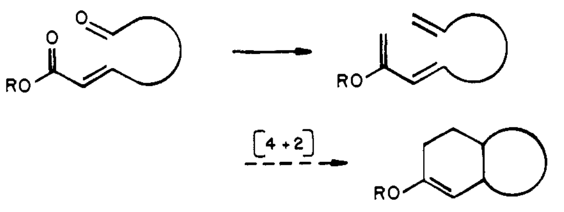

(3)

Diels-Alder reactions (eq 3). Related reactions with other carboxylic acid derivatives will be reported in due course.

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(5) The purity of **2** was assayed by ^{1}H NMR (C_6D_6) using a toluene internal standard and was obtained in a state of purity of 75% (by weight).[4] Toluene solutions of **2** under argon were prepared and assigned a "titer value" based upon the above ^{1}H NMR assay. Standardization of solution of **1** was also carried out by allowing a measured volume of the above solution to react with a measured quantity of methyl benzoate in an NMR tube under argon. Assuming a 1:1-reaction stoichiometry, the titer determined by this method was in agreement with the state of purity of the solid complex as ascertained by ^{1}H NMR.

(6) On sabbatical leave from the Department of Chemistry, California State University, Los Angeles, Calif.

(7) National Institutes of Health Postdoctoral Fellow.

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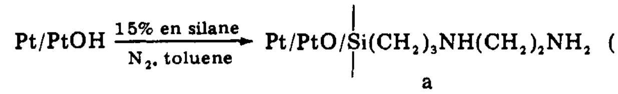
Can Chemical Reactivity Patterns on Chemically Modified Electrode Surfaces Be Anticipated from Solution Reactivity? A Study of Ruthenium Nitro Complexes

Sir:

Recent work[1] has shown that monolayers of electron-transfer couples immobilized on electrode surfaces via organosilane reagents undergo rapid electron transfer to and from the electrode. Such observations point to the possibility of linking homogeneous redox catalysis to heterogeneous electrocatalysis, by attaching reactive homogeneous catalysts to electrodes. Advantages gained would include the small amount of catalyst required, ready separability of products, and an electrode-controlled turnover rate. Central to this possibility is whether reactivity patterns of the homogeneous catalyst are preserved or usefully modified by its attachment to the electrode.

We have investigated the reactivity of immobilized ruthenium 2,2′-bipyridine (bpy) complexes which contain nitro or nitrosyl ligands and whose homogeneous chemistry[2,3] includes an example of oxidative catalysis.[3] Immobilization of the ruthenium nitro complex was achieved by silylamine functionalization of a Pt electrode[1a] surface (eq 1), followed by amide coupling[4] (eq 2). The $Ru^{II}NO_2$ electrodes I exhibit an electrochemical oxidation wave at $E_{\text{peak,anod}} = +1.08$ V vs. SSCE in acetonitrile attributable to oxidation of (typically) 1×10^{-10} mol/cm^2 of I (eq 3).



$$\text{Pt/PtOH} \xrightarrow[\text{N}_2\text{, toluene}]{\text{15\% en silane}} \underset{\text{a}}{\text{Pt/PtO/}\overset{|}{\underset{|}{\text{Si}}}\text{(CH}_2\text{)}_3\text{NH(CH}_2\text{)}_2\text{NH}_2} \quad (1)$$

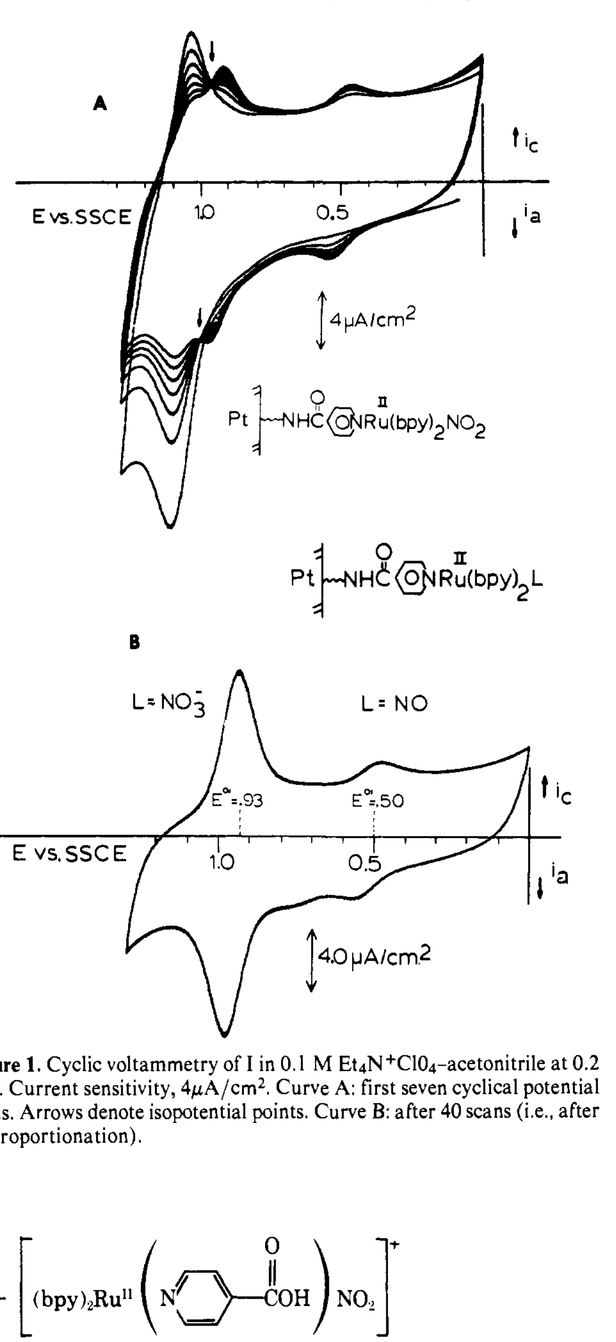
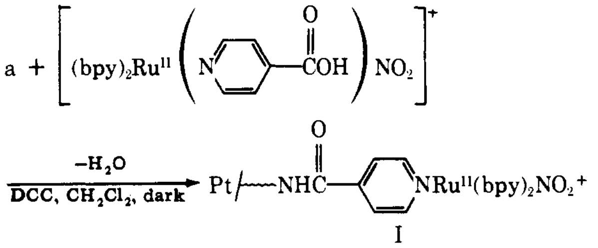
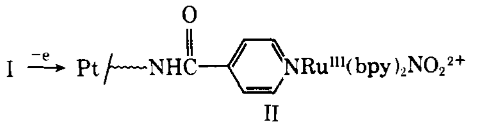


Figure 1. Cyclic voltammetry of I in 0.1 M $Et_4N^+ClO_4$-acetonitrile at 0.2 V/s. Current sensitivity, 4μA/cm^2. Curve A: first seven cyclical potential scans. Arrows denote isopotential points. Curve B: after 40 scans (i.e., after disproportionation).



(2)



(3)

Oxidation of the homogeneous solution analogue, $[(bpy)_2Ru^{II}(py)NO_2]^+$, occurs at $E_{\text{peak,anod}} = +1.06$ V vs. SSCE in acetonitrile, but the $Ru^{III}NO_2$ complex, $[(bpy)_2Ru^{III}(py)NO_2]^{2+}$, once formed is unstable and undergoes a net disproportionation at the nitro ligand[2a,b] (eq 4). Following oxidation, reversible cyclic voltammetric waves appear for the nitrato $[(bpy)_2Ru(py)ONO_2]^{2+/+}$ and nitrosyl $[(bpy)_2Ru(py)NO]^{3+/2+}$ complexes at $E^{\circ\prime} = +0.91$ and $+0.53$ V vs. SSCE, respectively.

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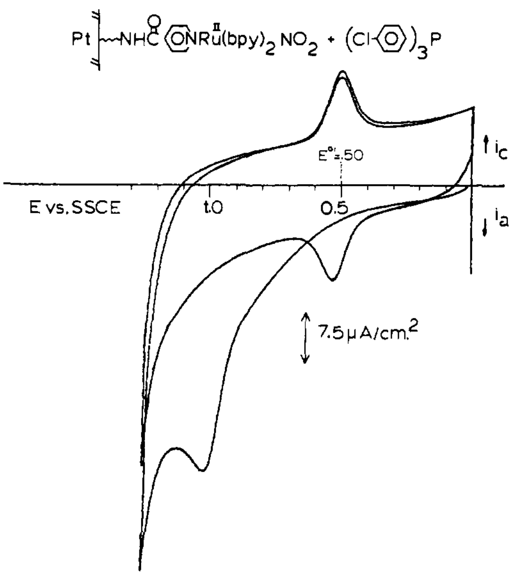
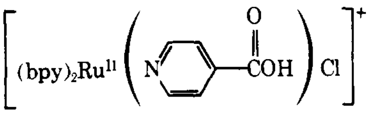


Figure 2. Cyclic voltammetry of I in 0.1 M $Et_4N^+ClO_4$-acetonitrile at 0.2 V/s in the presence of $(p\text{-}ClC_6H_4)_3P$.

$$2[(bpy)_2Ru^{III}(py)NO_2]^{2+} \xrightarrow{-1e} [(bpy)_2Ru^{III}(py)ONO_2]^{2+} + [(bpy)_2Ru^{II}(py)NO]^{3+} \quad (4)$$

The ligand disproportionation chemistry is deleterious in that it limits the scope of $[(bpy)_2Ru^{III}(py)NO_2]^{2+}$ as a homogeneous catalytic oxidant.[2a,b,3] A primary question in our immobilization experiments was whether this reactivity would be promoted or hopefully quenched on the electrode surface. Cyclic voltammetry of I at 0.2 V/s (Figure 1A), in contrast to the homogeneous solution results, shows a clearly defined reduction wave (reverse of eq 3) for the bound $Ru^{III}NO_2$ complex II at $E°' = +1.04$ V vs. SSCE. Ligand disproportionation still occurs, and the presence of isopotential points[5] (arrows) indicates that the decay of the reduction wave for II and appearance of that for the nitrato complex $Pt/{\sim}Ru^{III}ONO_2^{2+}$ at $E°' = +0.93$ V vs. SSCE are connected events on the time scale of Figure 1A. A preliminary kinetic analysis of the disappearance of II shows that its decay is first order and considerably slower than the analogous reaction in homogeneous solution. The net chemistry is also changed in that the ratio of immobilized nitrato to nitrosyl ($E°'_{surf} = 0.50$ V vs. SSCE), products, which is unity in the homogeneous solution case, varies somewhat from electrode to electrode but is in general >1:1 (Figure 1B). There may be an additional pathway in the immobilized state for the nitro → nitrato conversion involving loss of a second electron from II as shown in the reactivity scheme (Scheme I).

The effects of very low temperature on electron-transfer reactions at modified electrodes have not been explored. Wishing to use low-temperature cyclic voltammetry to better document the reaction mechanism and kinetics of the decay of immobilized I, we first examined cyclic voltammograms in 0.1 M $n\text{-}Bu_4NClO_4$-butyronitrile of the model complex b,



b

immobilized[1c] as in eq 2. No significant changes occur between +25 and −78 °C in peak shape, peak separation,[6] or the amount of transferred charge; i.e., the thermal barrier to electron transfer for the chloropyridine complex immobilized as in eq 2 is quite small.

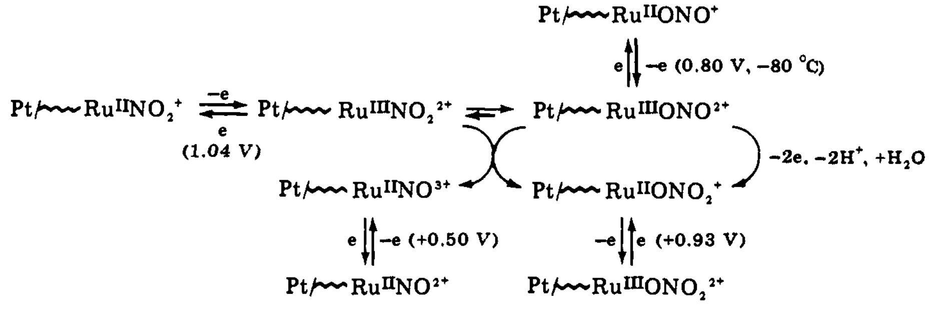
Low-temperature (−80 °C) electrochemistry of I, as might be expected, now shows a very persistent, reversible wave for the attached $Ru^{III}NO_2/Ru^{II}NO_2$ couple. Decay of the wave is still first order in $Ru^{III}NO_2$ (II), but it now occurs over a period of hours rather than tens of seconds. In addition, the low-temperature voltammetry experiments uncovered an intermediate with a reversible potential of $E°' = +0.80$ V. From associated experiments in homogeneous solution,[2a,e] we ascribe the new wave to the immobilized nitrito (O bound) couple $Ru^{III}ONO/Ru^{II}ONO$. The overall reaction scheme on the electrode surface Scheme I appears to be similar to that in homogeneous solution.[2b] One difference[7] which should be noted is the appearance of the one electron, outer-sphere oxidation of $Pt/{\sim}Ru^{II}ONO$ to the nitrato complex. This may intervene in the surface chemistry because of mobility restrictions on the oxygen atom transfer pathway which gives $Pt/{\sim}Ru^{II}NO$ and $Pt/{\sim}Ru^{II}ONO_2$ simultaneously. The low-temperature electrochemical results are notable in demonstrating that immobilization is effective for studying reaction mechanisms through the observation of intermediates. A complete mechanistic and kinetic description of immobilized disproportionation chemistry will be given in a full report.

A second reactivity comparision of note between homogeneous and immobilized $Ru\text{-}NO_2$ complexes is the nitro ⇄ nitrosyl interconversion

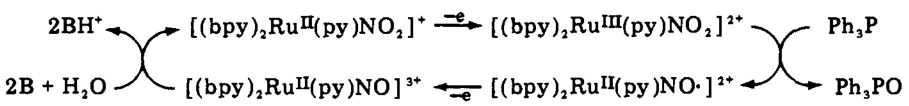
$$[(bpy)_2Ru^{II}(py)NO_2]^+ \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [(bpy)_2Ru^{II}(py)NO]^{3+} \quad (5)$$

which is known[2c,d] to be reversible in homogeneous solution. This chemistry also occurs for the immobilized complex. Brief exposure of an electrode I to acidic (HPF_6-acetonitrile) so-

Scheme I



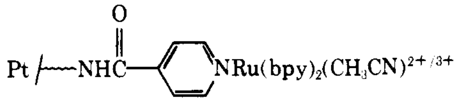
Scheme II



lution results in the appearance of the immobilized $RuNO^{3+/2+}$ wave. When the same electrode is exposed to a basic solution (lutidine–acetonitrile), the original $RuNO_2$ electrochemistry is regenerated, although slowly.

The third kind of immobilized complex reactivity is potentially the most significant since it relates to modified electrode electrocatalytic behavior. In solution, $[(bpy)_2Ru^{III}(py)NO_2]^{2+}$ has been shown[3] to act as a catalytic oxygen atom-transfer reagent toward triphenylphosphine to produce the corresponding phosphine oxide (Scheme II). The catalytic cycle shown can be driven electrochemically. The immobilized complex II shows similar catalytic properties. Figure 2 shows a cyclic voltammogram of I in the presence of tris(*p*-chlorophenyl)phosphine, in which the only observable[8] species remaining following a single oxidative potential sweep through the $Ru^{II}NO_2$ wave is the nitrosyl complex ($E°' = +0.50$ vs. SSCE). Since the yield of immobilized nitrosyl complex is nearly quantitative and little if any nitrato complex product is observable, the critical oxygen atom-transfer step on the chemically modified electrode surface competes effectively with the ligand oxidation steps in Scheme I. The direct electrode oxidation of $(p\text{-}ClC_6H_4)_3P$ on Pt in acetonitrile occurs at $E_{peak} = +1.49$ V vs. SSCE so that Figure 2 represents a catalytic shift in the phosphine electrolysis potential of 0.40 V.

Although the nitrosyl → nitro regeneration step is slow, the catalytic cycle suggested in Scheme II can be duplicated on the electrode surface. Catalytic currents are sustained upon phosphine, acetate ion, and trace amounts of water. There is the added complication, however, of solvolysis of II to give the acetonitrile complex[1e] c so that the catalysis is not persistent.



c

These results show that general forms of reactivity observed in homogeneous solution are reproducible, at least in qualitative detail for immobilized ruthenium nitro complexes. On the other hand, kinetic rates are substantially altered, favorably in the case of ligand oxidation but adversely for eq 5. The results point both to a need to develop a better understanding of the effects of immobilization on chemical kinetics, and of how electrode immobilization can be exploited in such studies.

Acknowledgment. This research was supported in part by grants from the National Science Foundation.

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(4) en silane is 3-(2-aminoethylamino)propyltrimethoxysilane, freshly distilled (Petrarch or PCR); DCC is *N,N'*-dicyclohexylcarbodiimide.

(5) D. F. Untereker and S. Bruckenstein, *Anal. Chem.*, **44**, 1009 (1972).

(6) Positive feedback resistance compensation was employed.

(7) Although not studied quantitatively, oxidation of $[(bpy)_2Ru(py)NO_3]^+$ by excess $[Ru(bpy)_3]^{3+}$ in acetonitrile also yields a nitrato to nitrosyl ratio of products of >1: J. L. Walsh, University of North Carolina, 1979, unpublished results. The oxidation by $[Ru(bpy)_3]^{3+}$ to give $[(bpy)_2Ru(py)NO_2]^{2+}$ is rapid and with excess $[Ru(bpy)_3]^{3+}$ an outer-sphere oxidation apparently competes with eq 4 to produce the nitrato product. On the surface, the excess outer-sphere oxidant may be either the electrode or attached $Ru^{III}NO_2$ or $Ru^{III}ONO$.

(8) We have not attempted an analysis for the presumed phosphine oxide product owing to the extremely small amounts produced in these experiments.

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Heteropoly Periodates: Structure of $[Co_4{}^{3+}I_3{}^{7+}O_{24}H_{12}]^{3-}$ Ion and Principles Pertinent to a Separate Potentially Important Category of Heteropoly Complexes

Sir:

This paper (a) reports the structure of $[Co_4{}^{3+}I_3{}^{7+}O_{24}H_{12}]^{3-}$ ion, determined by X-ray crystallography, and (b) explains how this combines with other data to indicate existence of a sizable and potentially important new category of heteropoly complexes made up of $I^{7+}O_6$ octahedra sharing O atoms with numerous lower charged transition metal atoms. Such heteropoly periodate species should easily form derivatives having organic ligands and should undergo condensations and cocondensations into cross-linked or linear polymers via polyfunctional ligands.

Only about five elements [Mo, W, and V in their higher oxidation states plus, to more limited extents, Ta(V) and Nb(V)] have been reported as functioning significantly in heteropoly species as "addenda" atoms (i.e., the positive-valent element(s) present in high atomic proportions).[1] Thus, essentially all known heteropoly complexes contain several atoms of one or more of these few elements,[1-3] although about 50 other elements function as heteroatoms.

This paper proposes that there are three main characteristics which atoms must have to become heteropoly addenda: (a) small size relative to the radius ratio indicated for octahedral packing with oxygens, (b) ability to change readily in solution between tetrahedral and octahedral coordination with O, and (c) high positive charge. It is proposed that I(VII) atoms, having these characteristics, can function as interesting heteropoly addenda.

The size criterion was elucidated by the X-ray crystal structure of $K_5[Co^{3+}W_{12}O_{40}]\cdot 20H_2O$,[1,4,5] the first heteropoly structure wherein all of the anion's oxygens were directly located. W–O distances for the exterior unshared O's average 1.68 Å, while 2.38 Å is the average distance between a W and the interior O trans to the unshared one. Similar marked displacements of addenda atoms from the centers of their respective octahedra toward exterior O atoms of polyanions have been confirmed in our laboratory[6,7] and elsewhere[3,8] in numerous subsequent more accurate determinations.

The fact that addenda atoms are decidedly small relative to the octahedral pockets which enclose them, so that they can move off-center, is of paramount importance in explaining the very existence of discrete polyanions with definite structures, as well as in explaining their unusual properties. Interior O atoms in polyanions are more or less surrounded by positively charged atoms and consequently are not excessively polarized in any one direction. In contrast, exterior unshared O atoms have as nearest neighbors only distinctly positively charged addenda atoms, and so those oxygens become heavily polarized, inward, toward the addenda atoms. This creates very strong ion-induced dipole terms, and the small addenda atoms are therefore located very close to the exterior unshared O atoms, which are themselves drawn tightly inward. Being very heavily polarized toward the center of the complex, the exterior O atoms are (1) very poor at attaching protons (so heteropoly

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