Comparison of the Catalytic Reduction of Dioxygen by [5,10,15,20-tetrakis((pentaammineruthenio(II))-4-pyridyl)porphyrinato]cobalt(II) in Solution and on Graphite Electrode Surfaces

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The [5,10,15,20-tetrakis((pentaammineruthenio(II))-4-pyridylporphinato]cobalt(II) complex that catalyzes the four-electron reduction of O_2 at graphite electrode surfaces on which it has been assembled has now been prepared in homogeneous solution. The preparative procedure for the catalyst is described, and the kinetics of its catalysis of the reduction of O_2 by chemical reductants in homogeneous solution are reported. In solution, only two-electron reductions of O_2 are obtained and the rate of intramolecular electron-transfer from the four $Ru(NH_3)_5$-py^{2+} centers on the periphery of the catalyst molecule to an O_2 molecule coordinated to the Co(II) center in the porphyrin ring is shown to be quite slow. Possible reasons for the contrasting mechanistic behavior of the catalyst in solution and on graphite electrodes are suggested.

In a series of recent reports from this laboratory, it was shown that the catalytic behavior of cobalt porphyrins toward the electroreduction of O_2 can be altered significantly by coordinating complexes of Ru(II) to ligand sites present on the periphery of the porphyrin ring.[1−6] In particular, certain of the cobalt porphyrins were converted from catalysts for the reduction of O_2 by two electrons into catalysts for the direct, four-electron reduction when three or more Ru(II) centers were coordinated to pyridine ligands on the porphyrin ring.[3] Because of difficulties encountered in attempts to obtain the desired coordination by means of reactions in solution, in previous studies the ruthenation of the porphyrins was carried out on the surface of graphite electrodes by reaction between the adsorbed porphyrin and $Ru(NH_3)_5OH_2^{2+}$[1−3,5,6] or $Ru(NH_3)_3(OH_2)_3^{2+}$[4] in solution. We have now devised a procedure for the preparation of solutions of the ruthenated cobalt porphyrin named in the title (hereafter $[CoP(pyRu(NH_3)_5)_4]^{8+}$ or CoPRu$_4$) which has allowed its catalytic activity to be examined in homogeneous solution. The outcome of such experiments is the subject of this report.

Araki and Toma have reported experiments in which tetrakis-(4-pyridyl)porphyrins were ruthenated in solution using $Ru^{III}(edta)OH_2^-$ (edta = ethylenediaminetetraacetate) or $Ru(bpy)_2$-Cl_2 (bpy = 2,2′-bipyridine) as the ruthenating reagents.[7−9] The cobalt porphyrin ruthenated with $Ru^{III}(edta)OH_2^-$ exhibited catalytic activity toward the reduction of O_2 that was not significantly different from that of the unruthenated cobalt porphyrin.[7,8] We obtained a similar result when the same cobalt porphyrin was adsorbed on graphite and ruthenated with $Ru^{III}(edta)OH_2^-$.[3] The contrasting, four-electron catalytic behavior obtained with $Ru(NH_3)_5OH_2^{2+}$ as the ruthenating agent

was one stimulus for the present study of the chemical reduction of O_2 in solution as catalyzed by dissolved [CoP(pyRu-$(NH_3)_5)_4]^{8+}$.

Experimental Section

Materials. $Ru(NH_3)_6^{2+}$, $Ru(NH_3)_5OH_2^{2+}$, $Ru(NH_3)_5Cl^{2+}$ and Ru-$(NH_3)_5py^{2+}$ were obtained from commercial sources or prepared as previously described.[2,5] Cobalt(II) was inserted into 5,10,15,20-tetrakis-(4-pyridyl) porphyrin (Strem Chemical Co.) by the conventional procedure.[10] Solutions were prepared from analytical grade reagents using laboratory deionized water that was further purified by passage through a purification train (MilliQ Plus).

Apparatus and Procedures. Electrochemical measurements were carried out with conventional cells and instrumentation. Electrodes were prepared from edge plane pyrolytic graphite (Union Carbide Co.) or glassy carbon (Tokai Electrode Co.), mounted with heat-shrinkable tubing and polished with 0.3 μm alumina on a moist polishing cloth or with 600 grit SiC paper. Potentials were measured and are quoted with respect to a saturated calomel reference electrode. Experiments were conducted at the ambient laboratory temperature 23 ± 1 °C.

The rates of the reduction of O_2 by complexes of Ru(II) in homogeneous solutions were measured, as in a previous report,[11] by observing the changes in the anodic current for the oxidation of Ru(II) to Ru(III) at a graphite disk electrode rotated at 1600 rpm and maintained at a potential (0.5 V) where no other electrode reactions occurred in 0.1 M CF_3COOH solutions continuously saturated with air and containing the soluble cobalt porphyrins as catalysts.

Preparation of $[CoP(pyRu(NH_3)_5)_4]^{12+}$ in Solution. In previous attempts to prepare solutions of the ruthenated tetrapyridylporphyrin by means of reaction 1 (pyH = $C_5H_5NH^-$) dark precipitates formed

$$CoP(pyH)_4^{4-} + 4Ru(NH_3)_5OH_2^{2+} \longrightarrow$$
$$CoP(pyRu(NH_3)_5)_4^{8+} + 4H^+ \quad (1)$$
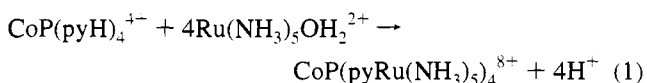
when sodium hydroxide was added to acidified solutions of the two reactants to adjust the pH from the low values required to keep the protonated form of the porphyrin in solution toward the higher pH values necessary to allow the $Ru(NH_3)_5OH_2^{2+}$ complex to compete with protons for coordination to the pyridine sites on the porphyrin ring.

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No useful products resulted from this preparative method. In addition, the extended reaction time required (many hours) made it desirable to maintain an excess of reducing agent in the reaction mixture to re-reduce the $Ru(NH_3)_5OH_2^{3+}$ formed by the $[CoP(pyH)_4]^{4+}$-catalyzed oxidation of $Ru(NH_3)_5OH_2^{2+}$ by any O_2 that leaked into the reaction vessel. Zn amalgam was a suitable initial reducing agent but it appeared to "deactivate" during lengthy reactions, especially when partial precipitation of the porphyrin occurred. The use of excess of the $Eu^{3+/2+}$ couple as a homogeneous redox mediator in conjunction with Zn(Hg) eliminated this source of difficulty. In the successful preparative procedure, 0.014 g (2 x 10^{-5} mol) of CoP(py)$_4$ was dissolved in 0.2 M CF_3COOH, the solution was filtered to remove any insoluble material and the filtrate was adjusted to a volume of 10.0 mL. A 0.1 g sample of $Eu_2(CO_3)_3$ was dissolved in the resulting solution, which was then deaerated by bubbling with argon and treated with 1 g of Zn(Hg) to reduce the Eu^{3+} to Eu^{2+}. After the reduction was complete (~30 min) 0.385 g (2 x 10^{-4} mol) of $[Ru(NH_3)_5Cl]Cl_2$ was added to the solution. The solid dissolved rapidly to produce a solution containing 20 mM $Ru(NH_3)_5OH_2^{2+}$. The resulting mixture was stirred under argon for about 12 h. The continuous reduction of protons by Zn(Hg) caused the pH of the mixture to increase slowly, and reaction 1 began to proceed as the concentration of protons decreased. As the pH approached 4−5, unreacted porphyrin began to precipitate from the solution. Aliquots (70−80 μL) of concentrated CF_3COOH were added to the mixture to redissolve the precipitates, and the reaction was allowed to continue. This process was repeated two or three times until samples withdrawn from the reaction mixture and analyzed by means of rotating disk voltammetry showed that substantial ruthenation of the porphyrin had occurred. At this point, a measured aliquot of the agitated mixture, including the precipitate, was transferred to a centrifuge tube. The precipitate was separated from the solution by centrifugation and washed several times with water. The washings were combined with the supernatant solution, and the mixture was diluted to 10.0 mL with 0.1 M CF_3COOH. The resulting solution was exposed to atmospheric O_2 for several hours during which the Ru(II), Co(II), and Eu(II) centers were oxidized to their +3 oxidation states. The concentration of the cobalt(III) porphyrin in the resulting solution was determined from its absorbance at 430 nm and the known molar absorbance of $[Co^{III}P(pyH)_4]^{5+}$ (ϵ = 2.14 x 10^5 M^{-1} cm^{-1}).[12] The justification for using this value of ϵ for the non-ruthenated porphyrin was the report of Toma and Araki[7] that the value of ϵ for the Soret band of $[Fe^{III}P(pyRu(edta))_4]^{3-}$ matched that for $[Fe^{III}P(pyCH_3)_4]^{5+}$ (pyCH$_3$ = $C_5H_5NCH_3^+$)[13] and the fact that the ϵ values of $[Co^{III}P(pyH)_4]^{5+}$ and $[Co^{III}P(pyCH_3)_4]^{5+}$ are the same in the Soret region.[12]

Results

Electrochemical Assay of Solutions of the Ruthenated Porphyrin. The quantities of $Ru(NH_3)_5^{3+}$ groups coordinated to porphyrin molecules that were subjected to the preparative procedure described in the Experimental Section were determined from voltammograms recorded at a rotating disk electrode in aliquots of the preparation solution after its oxidation with O_2 was completed. A typical voltammogram is shown in the solid curve in Figure 1A. The prominent wave with $E_{1/2}$ = −0.17 V corresponds to the reduction of the excess $Ru(NH_3)_5-OH_2^{3+}$ that was not coordinated to the pyridine ligands of CoP-(py)$_4$ during the preparation. The difference between the plateau current for this wave and that resulting when the same procedure was carried out in the absence of CoP(py)$_4$ (dashed curve in Figure 1A) was used to calculate the quantity of $Ru(NH_3)_5-OH_2^{2+}$ that had reacted with CoP(py)$_4$. The results of such analyses for several preparative runs are summarized in Table 1. These data show that the procedure described in the Experimental Section produces solutions that contain the tetraruthenated porphyrin, $[Co^{II}P(pyRu^{II}(NH_3)_5)_4]^{8+}$ or $[Co^{III}P-(pyRu^{III}(NH_3)_5)_4]^{13+}$.

The smaller wave near 0.085 V in the solid curve in Figure 1A corresponds to the reduction of the $Ru(NH_3)_5^{3+}$ centers
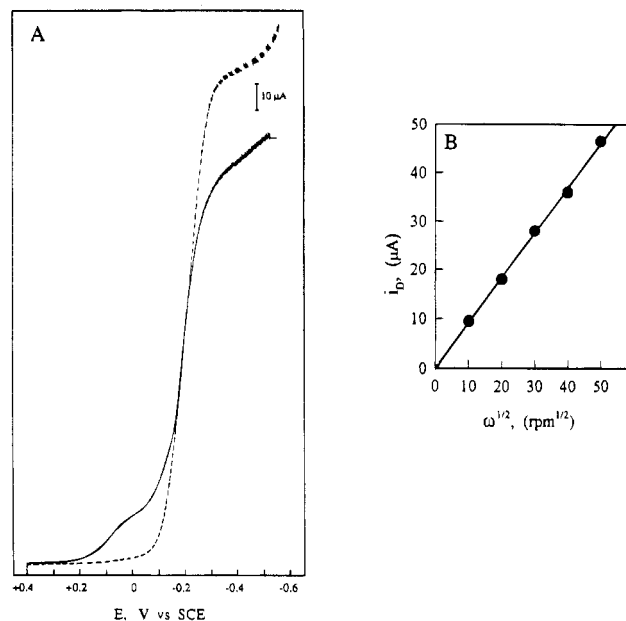

Figure 1. (A) Rotating disk voltammetry of a solution obtained from the reaction between $[CoP(pyH)]^{4+}$ and $Ru(NH_3)_5OH_2^{2+}$ followed by air oxidation (solid curve). The dashed curve is the response obtained when the reaction procedure (see Experimental Section) was carried out in the absence of $[CoP(pyH)_4]^{4+}$. Supporting electrolyte: 0.1 M CF_3COOH deaerated by bubbling with argon. Rotation rate = 100 rpm. (B) Levich plot of the plateau current for the smaller wave in (A) vs the electrode (rotation rate)$^{1/2}$.

Table 1. Stoichiometric Composition and Diffusion Coefficients of the Product Resulting from the Reaction of CoP(py)$_4$ and Excess $Ru(NH_3)_5OH_2^{2+}$ [a]

expt. no.	$[Ru]_0$,[b] mM	$[Ru]_f$,[c] mM	$10^2[CoP]_{tot}$,[d] mM	Ru/Co[e]	$10^6 D_f$[f] cm^2 s^{-1}
1	2.01	1.76	6.50	3.85	1.35
2	1.94	1.48	11.7	3.93	1.35
3	2.00	1.87	3.33	3.90	1.43
4	1.86	1.40	11.0	4.18	1.48

[a] The reaction conditions and procedures are described in the Experimental Section. [b] The initial concentration of $Ru(NH_3)_5OH_2^{2+}$ in the reaction solution. [c] The concentration of $Ru(NH_3)_5OH_2^{2+}$ present in the solution when the reaction was terminated as evaluated in the oxidized solution from the plateau current for the reduction of $Ru(NH_3)_5OH_2^{3+}$ at a rotating disk electrode. [d] Total concentration of (all forms of) cobalt tetrapyridylporphyrin in the solution after the reaction was terminated. Evaluated from the absorbance at 430 nm using log ϵ = 5.33. [e] Number of $Ru(NH_3)_5^{2+}$ centers coordinated to each CoP(py)$_4$ molecule calculated as $([Ru]_0 - [Ru]_f)/[CoP]_{tot}$. [f] Diffusion coefficient of $[Co^{III}P(pyRu(NH_3)_5)_4]^{13+}$ calculated from the plateau current of the first wave of the current−potential curve such as the solid curve in Figure 1.

coordinated to the pyridine ligands of the porphyrin. This assignment is based on the close correspondence between the half-wave potential for this wave and that of the $Ru(NH_3)_5py^{3+/2+}$ couple measured separately (Potentials in the same vicinity have been reported in various supporting electrolytes.[14]) A wave at the same potential was also obtained when the preparative procedure was repeated using tetrapyridylporphyrin with no cobalt in the ring. The concentration of $Ru(NH_3)_5py^{3+}$ centers, determined by the method just described, was used to evaluate the diffusion coefficient of the $[Co^{III}P(pyRu(NH_3)_5)_4]^{13+}$ complex from the magnitude of the plateau current of the smaller wave in Figure 1A using the Levich equation.[15] That the plateau

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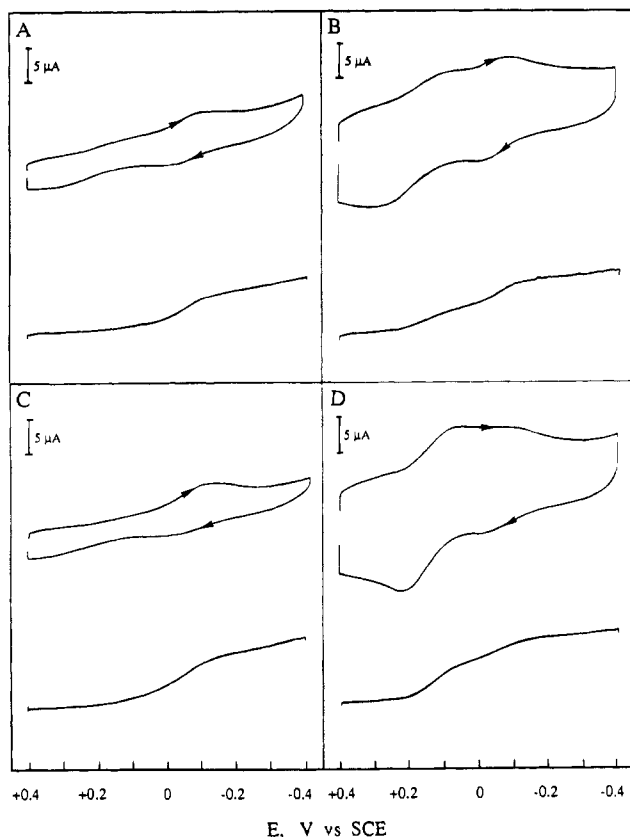
Figure 2. Voltammetry of 0.36 mM [Co^{III}P(pyH$^+$)$_4$]$^{5+}$ at 0.20 cm^2 glassy carbon (A, C) or 0.32 cm^2 edge plane pyrolytic graphite (B, D) electrodes: upper curves, cyclic voltammetry at a scan rate of 50 mV s^{-1}; lower curves, rotating disk voltammetry at a rotation rate of 100 rpm and a potential scan rate of 5 mV s^{-1}. Supporting electrolyte: (A, B) 0.1 M CF$_3$COOH; (C, D) 1 M CF$_3$COOH.

currents adhered to the Levich equation is demonstrated by the plot in Figure 1B. The average value of the diffusion coefficient obtained, 1.4 × 10^{-6} cm^2 s^{-1}, is somewhat smaller than the value reported for [Co^{III}P(pyCH$_3$)$_4$]$^{5+}$, 2.2 × 10^{-6} cm^2 s^{-1},[12] as would be expected for the larger, more highly charged cation. The reasonable value of the diffusion coefficient obtained in this way provided additional support for the conclusion that the species responsible for the wave at 0.085 V in the solid curve of Figure 1A is the fully ruthenated [Co^{III}P(pyRu(NH$_3$)$_5$)$_4$]$^{13+}$ complex.

The preparative procedure given in the Experimental Section typically resulted in the conversion of 50—60% of the initial CoP(py)$_4$ into the tetraruthenated product. The porphyrin that precipitated and was separated from the reaction product must have remained largely unruthenated on the basis of the data in Table 1. We speculate that the greater solubility of partially ruthenated porphyrins facilitates their further reaction with the excess Ru(NH$_3$)$_5$OH$_2$$^{2+}$ present in the reaction solution, which could account for the observation that the preparative procedure leads primarily to the production of the fully ruthenated or the completely unruthenated porphyrin.

Electrochemistry of CoP(py)$_4$ before Ruthenation. The electrochemical response exhibited by the Co(III)/Co(II) couple of [Co^{III}P(pyH)$_4$]$^{5+}$ dissolved in aqueous acid depends upon the electrode material and somewhat upon the acidity of the supporting electrolyte. At glassy carbon (GC) electrodes a prominent, quasi-reversible response is obtained at −0.05 V (Figure 2A,C). There is also a very weak reversible response near 0.1 V. The latter response becomes the dominant one at edge plane pyrolytic graphite (EPG) electrodes as shown in Figure 2B,D. The presence of two waves in voltammograms

for Co^{III}P(pyH)$_4$$^{5+}$ has been reported in a previous study,[16] but the origin of the second wave is uncertain. Adsorption of the porphyrins occurs on both electrode surfaces, but neither response can be attributed solely to adsorbed reactant because both responses are also present in steady-state rotating disk voltammograms recorded at scan rates too low to produce a significant contribution from the adsorbed reactant (lower set of curves in Figure 2). The dependence of the responses on the acidity of the solution (Figure 2) and the presence of only a single, acid-independent response from the corresponding tetra-*N*-methylated porphyrin, [Co^{III}P(pyCH$_3$)$_4$]$^{5+}$,[12,17] suggest that both monomeric and aggregated porphyrins may be present in solutions prepared by dissolving CoP(py)$_4$ in aqueous acid. The two types of porphyrin could well exhibit different formal potentials for the Co(III)/Co(II) couple, and the aggregate might monomerize with increasing acidity as its net charge increased to match that of the apparently nonaggregated [Co^{III}P-(pyCH$_3$)$_4$]$^{5+}$. We presume that the tetraruthenated pyridylporphyrin would resemble the tetramethylated pyridylporphyrin in exhibiting a single Co(III)/Co(II) response at a potential near 0.1 V.

On the basis of the voltammograms in Figure 2, the potential where the Co(III) center of the [Co^{III}P(pyRu(NH$_3$)$_5$)$_4$]$^{13+}$ complex is reduced to Co(II) at EPG electrodes is likely to be too close to the potential where the Ru(NH$_3$)$_5$py^{3+} centers are reduced to produce separate waves for the two processes. Thus, the plateau current of the wave near 0.085 V in Figure 1A would correspond to the reduction of each molecule of the complex by five electrons. This was the value of *n* used in applying the Levich equation[15] to calculate the diffusion coefficients of [Co^{III}P(pyRu(NH$_3$)$_5$)$_4$]$^{13+}$ listed in Table 1.

Catalysis of the Electroreduction of O$_2$ by [Co^{III}P(pyRu-(NH$_3$)$_5$)$_4$]$^{13+}$ Adsorbed on the Electrode Surface. The cyclic voltammetry of a solution containing a mixture of [Co^{III}P(pyRu-(NH$_3$)$_5$)$_4$]$^{13+}$ and Ru(NH$_3$)$_5$OH$_2$$^{3+}$ recorded at an EPG electrode in the absence or presence of O$_2$ is shown in Figure 3A. In the absence of the tetraruthenated cobalt porphyrin, the reduction of O$_2$ occurs at much more negative potentials (solid curve in Figure 3B) so the catalysis of the reduction by the porphyrin complex is apparent. The dissolved porphyrin spontaneously adsorbs on the electrode surface as shown by the response obtained when the electrode from Figure 3A was transferred to pure supporting electrolyte (dashed curve in Figure 3C). The catalysis of the reduction of O$_2$ by the adsorbed porphyrin is also shown (solid curve in Figure 3C). The EPG electrode used to obtain the voltammograms in Figure 3A,C had been polished with 0.3 μm alumina. The spontaneous absorption of [CoP-(pyRu(NH$_3$)$_5$)$_4$]$^{13+}$ on the resulting surface produced a smaller quantity of adsorbed porphyrin than had been employed in our previous studies where larger quantities of CoP(py)$_4$ were deposited on the electrode surface and ruthenated in place.[1-3] To obtain comparable quantities of adsorbed, ruthenated porphyrin by spontaneous adsorption from solution, the EPG electrode was polished (abraded) with No. 600 SiC paper which produced a less smooth surface. Adsorption from the solution used in Figure 3A was about twice as large on the resulting electrode surface, and transfer to pure supporting electrolyte produced the responses shown in Figure 3D. These voltammograms closely resemble those obtained in our previous studies in which comparable quantities of the tetraruthenated porphyrin were prepared on the electrode surface.[2,3]

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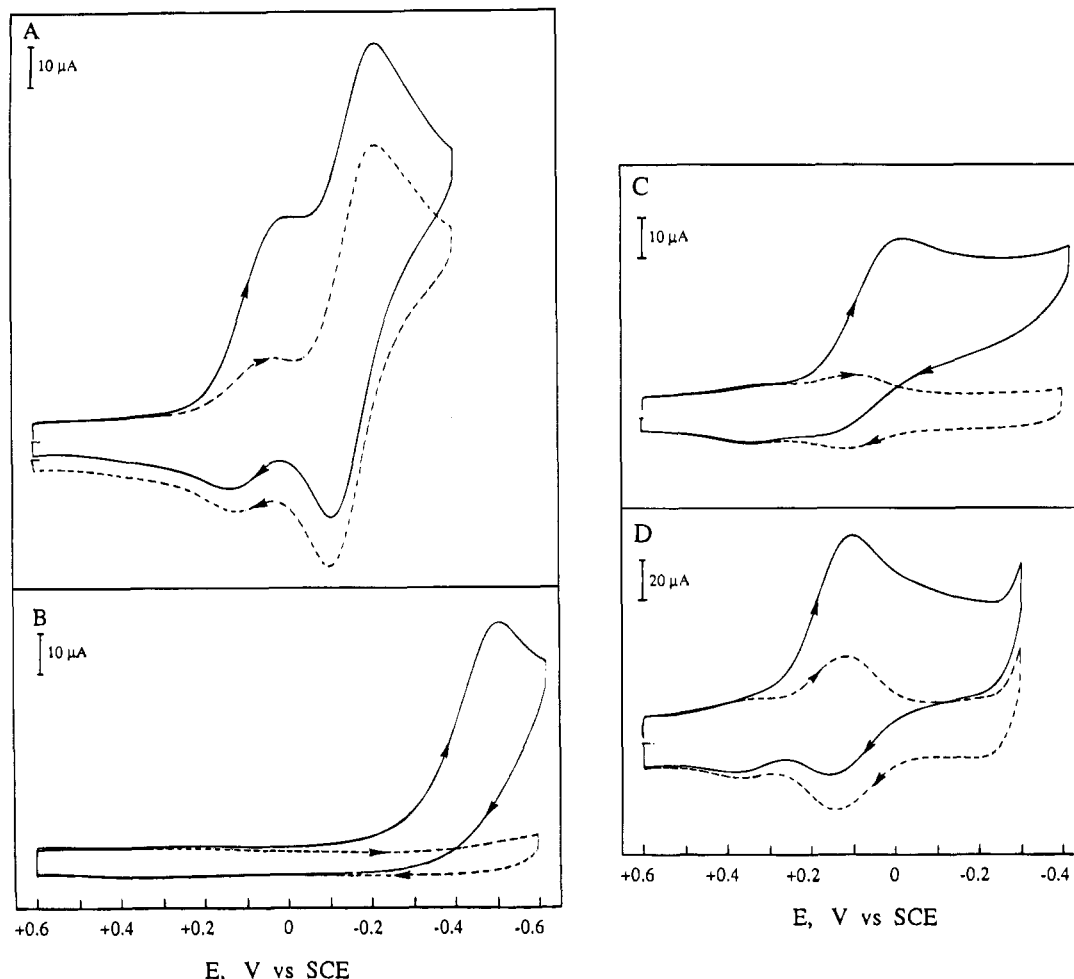
Figure 3. (A) Cyclic voltammetry of a mixture of 0.46 mM $[Co^{III}P(pyRu(NH_3)_5)_4]^{13+}$ and 1.5 mM $Ru(NH_3)_5(OH_2)^{3+}$ in the absence (dashed curve) and the presence (solid curve) of O_2. Supporting electrolyte: 0.1 M CF_3COOH. Scan rate: 50 mV s^{-1}. (B) Reduction of O_2 at an EPG electrode in pure supporting electrolyte. The dashed curve is the background response recorded in the absence of O_2. Other conditions was as in (A). (C) Responses obtained when the electrode used to record the voltammogram in (A) was transferred to pure supporting electrolyte containing no O_2 (dashed curve) or saturated with air (solid curve). The area under the peak in the dashed curve corresponds to 9×10^{-11} mol cm^{-2} of adsorbed porphyrin. Other conditions were as in (A). (D) Repeat of (C) with an EPG electrode polished with No. 600 SiC paper instead of alumina. The quantity of porphyrin adsorbed on the electrode was 5.7×10^{-10} mol cm^{-2}.

To determine the stoichiometry of the electroreduction of O_2 by the adsorbed porphyrin, an electrode like the one used to record Figure 3D was employed as a rotating disk electrode in solutions saturated with air. The slope of a Koutecky–Levich plot[18] of the (plateau current)$^{-1}$ vs the electrode (rotation rate)$^{-1/2}$ matched that in our previous studies[1-3] which corresponded to the four-electron reduction of O_2. Thus, the ruthenated porphyrin prepared in homogeneous solution and adsorbed on the electrode yields comparable catalytic currents and exhibits the same catalytic stoichiometry as that obtained when the porphyrin was preadsorbed on the electrode and ruthenated by the heterogeneous coordination reaction.

The reduction of O_2 was also examined with a rotating graphite disk-platinum ring electrode (as in our previous studies[1-3]). The $[Co^{III}P(pyRuNH_3)_5)_4]^{13+}$ catalyst was adsorbed on the disk, and the platinum ring was held at 1.0 V to detect any H_2O_2 produced during the reduction of O_2 at the disk electrode. The responses obtained at the disk and ring electrodes are shown in Figure 4. Anodic ring current begins to flow as the reduction of O_2 at the disk electrode commences, but the ring current passes through a maximum and decreases to a low,

steady value when the disk current reaches its plateau. The ratios of the ring to disk currents correspond to the four-electron reduction of 90% of the O_2 molecules on the plateau of the disk current–potential curve and to 78% of the O_2 molecules at the disk potential corresponding to the maximum in the ring current. The behavior shown in Figure 4 can be understood by comparison with the current–potential curve for the adsorbed catalyst in the absence of O_2, shown by the dashed curve in Figure 4. The catalyzed reduction of O_2 at the disk begins before all of the Ru(III) centers of the adsorbed ruthenated porphyrin are reduced to Ru(II), and under these conditions more of the O_2 is reduced to H_2O_2 than is true at more negative disk potentials where all of the adsorbed porphyrin is in the fully reduced state that is most active in catalyzing the four-electron reduction of O_2.

Stoichiometry of the Chemical Reduction of O_2 by Complexes of Ru(II) in Solution. When the $[Co^{II}P(pyRu(NH_3)_5)_4]^{8+}$ complex is adsorbed on the surface of graphite electrodes, the electrons required for the electroreduction of O_2 can be supplied by the electrode. Indeed, that is the mechanism by which the adsorbed, ruthenated porphyrin is believed to catalyze the four-electron electroreduction of O_2 to H_2O.[3] It was of interest to determine if this catalyst achieved the same four-electron reduction when it was dissolved in solution and used to catalyze the reduction of O_2 by chemical reducing

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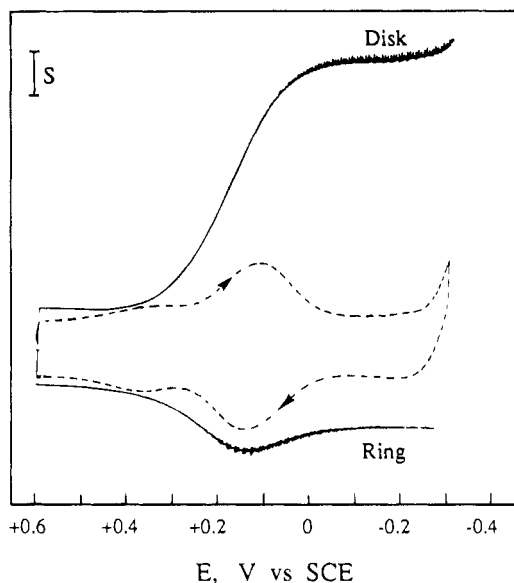
Figure 4. Current—potential curves for the catalyzed reduction of O_2 at a rotating pyrolytic graphite disk—platinum ring electrode. The disk was coated with 6×10^{-10} mol cm^{-2} of $[Co^{III}P(pyRu(NH_3)_5)_4]^{13+}$ by spontaneous adsorption from a solution of the complex. The Pt ring electrode was maintained at 1.0 V as the disk electrode potential was scanned at 5 mV s^{-1}. Supporting electrolyte: 0.5 M $HClO_4$ saturated with air. Electrode rotation rate: 100 rpm. The dashed curve is the cyclic voltammetric response of the adsorbed porphyrin in the absence of O_2 recorded at a scan rate of 50 mV s^{-1}. Current scale: $S = 10 \mu A$ for the disk and the dashed curve; $S = 2 \mu A$ for the ring.

agents. To do so, solutions containing low concentrations of $[Co^{III}P(pyH)_4]^{5+}$ or $[Co^{III}P(pyRu(NH_3)_5)_4]^{13+}$ were prepared in deaerated solutions of 0.1 M CF_3COOH of measured volume. (Solutions of the latter complex also contained $Ru(NH_3)_5OH_2^{3+}$ because of the excess of the $Ru(NH_3)_5OH_2^{2+}$ complex present during the preparation of the ruthenated porphyrin). $Ru(NH_3)_6^{2+}$ or $Ru(NH_3)_5py^{2+}$ was injected into the deaerated solution of the catalyst, and the steady plateau current for the oxidation of Ru(II) (typically 0.1 mM) to Ru(III) was monitored at a rotating graphite disk electrode maintained at 0.5 V, where no other electrode reactions occur. Next, a measured aliquot of air- or O_2-saturated supporting electrolyte was injected into the mixture, and the resulting decrease in the Ru(II) concentration was monitored until the anodic current arising from the oxidation of the remaining Ru(II) complex became stable again. The stoichiometry of the porphyrin-catalyzed, homogeneous reduction of O_2 by the Ru(II) complex was determined from the change in the concentration of the Ru(II) complex calculated from the measured decrease in the anodic current for its oxidation. In Figure 5 are shown the current—time transients obtained in several experiments of this type. When no catalyst is present (Figure 5A) the concentration of Ru(II) ($Ru(NH_3)_6^{2+}$) changes only gradually because its uncatalyzed reaction with O_2 is slow.[19] With $[Co^{II}P(pyH)_4]^{4+}$ as catalyst, the reaction between the reductant and O_2 is somewhat faster for $Ru(NH_3)_6^{2+}$ (Figure 5B) than for $Ru(NH_3)_5py^{2+}$ (Figure 5C), but the stoichiometry of the catalyzed reaction is the same for both reductants and corresponds to the reduction of O_2 to H_2O_2. With $[Co^{II}P(pyRu(NH_3)_5)_4]^{8+}$ as the catalyst (Figure 5D), the reaction rate is higher but the stoichiometry again corresponds to two electrons per O_2 molecule. Similar measurements were also made with solutions in which the $[Co^{II}P(pyRu(NH_3)_5)_4]^{8+}$ complex was the only reducing agent present. In this case, the complex acted as both catalyst and reductant. The diffusion
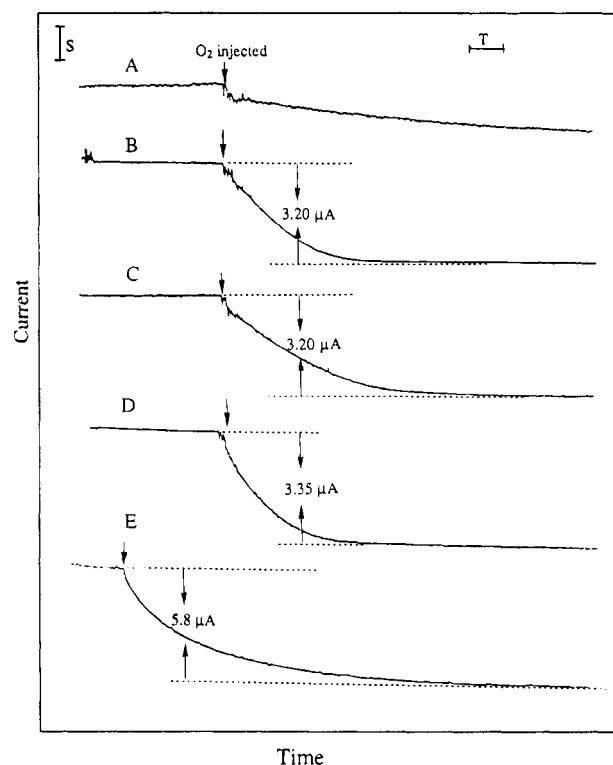
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Figure 5. Changes in the anodic current for the oxidation of Ru(II) at a rotating graphite disk electrode produced by the addition of a measured quantity of O_2 to the solutions. The electrode, maintained at a potential of 0.5 V, was rotated at 1600 rpm. Solution compositions, 0.1 M CF_3-COOH plus: (A) 0.1 mM $Ru(NH_3)_6^{2+}$; (B) 0.1 mM $Ru(NH_3)_6^{2+}$ + 0.005 mM $[CoP(pyH_4)]^{4+}$; (C) 0.1 mM $Ru(NH_3)_5py^{2+}$ + 0.005 mM $[CoP(pyH_4)]^{4+}$; (D) 0.1 mM $Ru(NH_3)_6^{2+}$ + 0.005 mM $[CoP(pyRu-(NH_3)_5)_4]^{8+}$ + 0.08 mM $Ru(NH_3)_5OH_2^{3+}$; (E) 0.024 mM $[CoP(pyRu-(NH_3)_5)_4]^{8+}$ + 0.38 mM $Ru(NH_3)_5OH_2^{3+}$. The arrows mark the point at which 500 μL aliquots of 0.1 M CF_3COOH containing 0.14 (A, B, C, D) or 0.70 (E) μmol of O_2 were injected into the solutions. The solution volume was 20 mL. The initial anodic currents were 23 μA (A, B, C, D) and 8 μA (E). Current scale: $S = 1 \mu A$ (A, B, C, D); 1.66 μA (E). Time scale: $T = 10$ s (A, B, C, D), 31.3 s (E).

coefficient of the $[Co^{II}P(pyRu(NH_3)_5)_4]^{8+}$ complex is about one-fifth as large as that of $Ru(NH_3)_6^{2+}$ so that much smaller anodic currents were obtained at the rotating disk electrode and larger quantities of O_2 were injected into the solutions to improve the precision in the measurements of the resulting changes in the Ru(II) oxidation currents. A typical result, shown in Figure 5E, also corresponds to the reduction of O_2 by only two electrons. Thus, the tetraruthenated cobalt porphyrin that catalyzes the four-electron reduction when it is adsorbed on the surface of graphite electrodes accomplishes only the two-electron reduction of O_2 when it is dissolved in solutions containing chemical reductants whether they are one-electron reductants ($Ru(NH_3)_6^{2+}$, $Ru(NH_3)_5py^{2+}$) or potential four-electron reductants $[Co^{II}P(pyRu(NH_3)_5)_4]^{8+}$. It should be noted that neither $[CoP(pyH_4)]^{4+}$ nor $[CoP(pyRu(NH_3)_5)_4]^{8+}$ catalyzes the reduction of H_2O_2 either when in solution or when adsorbed on electrodes. Injection of H_2O_2 instead of O_2 into the solutions of Figure 5 produced no comparable changes in current.

Kinetics of the Homogeneous Reduction of O_2 by Ru(II) Complexes. In order to examine more fully the differences in the behavior of the dissolved and adsorbed cobalt porphyrins as catalysts for the reduction of O_2, the kinetics of the reduction of O_2 by $Ru(NH_3)_6^{2+}$ or $Ru(NH_3)_5py^{2+}$ as catalyzed by $[CoP(pyH_4)]^{4+}$ or $[CoP(pyRu(NH_3)_5)_4]^{8+}$ were measured, as in a previous report,[11] by using a rotating disk electrode to monitor the concentration of Ru(II) as a function of time after a small amount was injected into solutions continuously saturated with
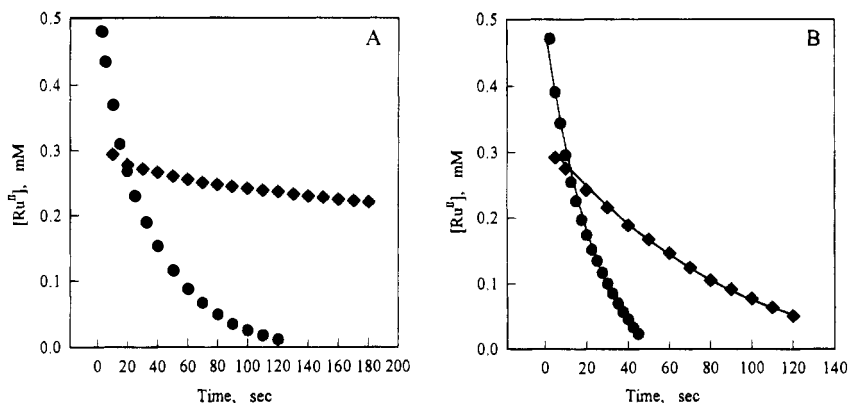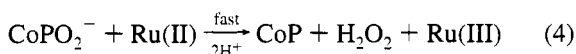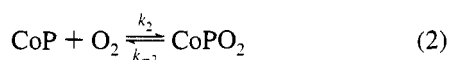
Figure 6. Kinetic data for the homogeneous reduction of O_2 by Ru(II) in the absence of a catalyst (A) or as catalyzed by 5×10^{-6} M $[CoP(pyH)_4]^{4+}$ (B). Supporting electrolyte: 0.1 M CF_3COOH continuously saturated with air: $[O_2] = 0.28$ mM. Ru(II) reductant and its initial concentration: 0.47 mM $Ru(NH_3)_6^{2+}$ (●); 0.31 mM $Ru(NH_3)_5py^{2+}$ (◆). The points are experimental, and in (B) the lines were calculated from eq 8 using the values of k_2, k_5, and k_3/k_{-2} given in Table 2A.

Table 2. Kinetic Parameters for the Homogeneous Oxidation of Ru(II) by O_2 As Catalyzed by $[CoP(pyH)_4]^{4+}$ or $[CoP(pyRu(NH_3)_5)_4]^{8+}$ [a]
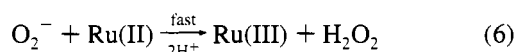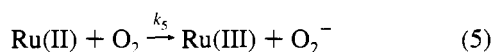
A. $[CoP(pyH_4)]^{4+}$ as Catalyst[b]

reductant	$[Ru^{II}]_0$, mM	k_5,[c] M^{-1} s^{-1}	k_2,[d] M^{-1} s^{-1}	k_3/k_{-2},[d] M^{-1}
$Ru(NH_3)_6^{2+}$	0.47	53	2.7×10^3	1.2×10^4
$Ru(NH_3)_5py^{2+}$	0.31	1.9	2.6×10^3	2.8×10^3

B. $[(CoP(pyRu(NH_3)_5)_4]^{8+}$ as Catalyst

reductant	$[Ru^{II}]_0$, mM	k_5,[c] M^{-1} $s-1$	k_2,[e] M^{-1} s^{-1}	$k_3/(k_{-2} + k_9)^e$ M^{-1}	k_2k_9/k_3,[e] s^{-1}
$Ru(NH_3)_6^{2+}$	0.42^b	53	1.9×10^4	2.6×10^3	<1
$Ru(NH_3)_5py^{2+}$	0.31^b	1.9	1.9×10^4	1.4×10^3	<1
$[CoP(pyRu(NH_3)_5)_4]^{8+}$	0.18^f	1.9^g	1.7×10^4	71	<1

[a] Supporting electrolyte was 0.1 M CF_3COOH saturated with air ($[O_2] = 0.28$ mM). [b] Catalyst concentration was 5×10^{-6} M. [c] Measured from a pseudo-first-order kinetic plot obtained in the absence of catalyst. [d] Obtained by non-linear least-squares fitting of the experimental data to eq 8. The values are the averages obtained in three or more experimental runs. Individual values typically differed by less than 15%. [e] Obtained by nonlinear least-squares fitting of the experimental data to eq 12 or by using Kinsim.[20] Data from at least three experimental runs were employed in each case. Agreement from run to run was typically ±10%. The two procedures produced closely similar parameters. The values listed are the average of the pairs of values obtained by the two procedures. [f] The catalyst concentration was assumed to remain constant and equal to $[Ru^{II}]_0/4$. [g] The value of k_5 was assumed to be the same as the value measured with $Ru(NH_3)_5py^{2+}$ as reductant.

air. Shown in Figure 6A are kinetic data obtained with Ru-$(NH_3)_6^{2+}$ or $Ru(NH_3)_5py^{2+}$ as the reductant in the absence of catalyst, and in Figure 6B are the corresponding data with CoP-$(pyH_4)^{4+}$ or $[CoP(pyRu(NH_3)_5)_4]^{8+}$ as the catalyst. The acceleration of the reaction rate by the dissolved porphyrins is apparent. To obtain a quantitative comparison of the reaction rates, the relevant kinetic rate laws were applied. The mechanism previously described for the cobalt porphyrin-catalyzed homogeneous reduction of O_2 is given in reactions 2−4,[11] where

$$CoP + O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CoPO_2 \tag{2}$$

$$CoPO_2 + Ru(II) \overset{k_3}{\longrightarrow} CoPO_2^- + Ru(III) \tag{3}$$

$$CoPO_2^- + Ru(II) \xrightarrow[2H^+]{fast} CoP + H_2O_2 + Ru(III) \tag{4}$$

CoP is the cobalt porphyrin catalyst. The uncatalyzed reduction (reactions 5 and 6) proceeds in parallel with reactions 2−4.

$$Ru(II) + O_2 \overset{k_5}{\longrightarrow} Ru(III) + O_2^- \tag{5}$$

$$O_2^- + Ru(II) \xrightarrow[2H^+]{fast} Ru(III) + H_2O_2 \tag{6}$$

Equation 7 is the rate law that applies to the mechanism depicted in reactions 2−6 using the steady-state assumption for the concentration of $CoPO_2$. Integration of eq 7 for the case where

$$-\left(\frac{d[Ru^{II}]}{dt}\right) = -2\left(\frac{d[O_2]}{dt}\right) =$$

$$2[O_2][Ru^{II}]\left\{\frac{k_2k_3[CoP]}{k_3[Ru^{II}] + k_{-2}} + K_5\right\} \tag{7}$$

the concentrations of CoP and O_2 are constant leads to the analytical solution given in eq 8, where $y = k_2[CoP] +$

$$\frac{1}{k_5}\ln\left\{\frac{y + k_5[Ru^{II}]}{y + k_5[Ru^{II}]_0}\right\} - \frac{k_{-2}}{k_3y}\ln\left\{\frac{[Ru^{II}]_0 \, (y + k_5[Ru^{II}])}{[Ru^{II}](y + k_5[Ru^{II}]_0)}\right\} =$$

$$-2[O_2]t \tag{8}$$

k_5k_{-2}/k_3, $[Ru^{II}]_0$ is the initial concentration of Ru(II), and $[Ru^{II}]$ is its concentration at time t. Kinetic data such as those in Figure 6B were fit to eq 8 by a nonlinear regression using the values of k_5 measured in the absence of CoP and varying k_2 and k_3/k_{-2} to obtain the best agreement with the experimental data. The results, plotted as the lines in Figure 6B, produced the values of k_2 and k_3/k_{-2} listed in Table 2A. The values with $Ru(NH_3)_6^{2+}$ as the reductant are similar to those reported previously when cobalt tetrakis(N-methylpyridiniumyl)porphyrin was used as the catalyst.[11] The smaller value of k_3/k_{-2} obtained with $Ru(NH_3)_5$-py^{2+} as the reductant is the result expected for a slower electron transfer by the weaker reductant. ($E^i = -0.19$ and $+0.065$ V for the $Ru(NH_3)_6^{3+/2+}$ and $Ru(NH_3)_5py^{3+/2+}$ couples, respectively.[14])
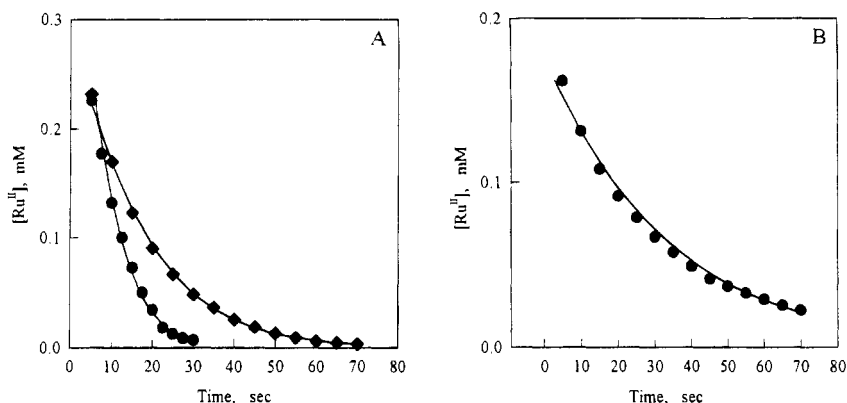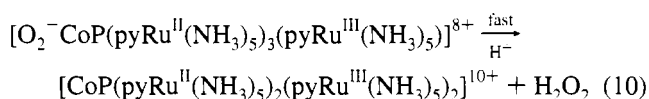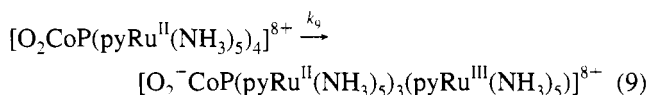
Figure 7. (A) Kinetic data for the homogeneous reduction of O_2 by $Ru(NH_3)_6{}^{2+}$ (●) or $Ru(NH_3)_5py^{2+}$ (◆) as catalyzed by $[CoP(pyRu(NH_3)_5)_4]^{8+}$. The points are experimental, and the lines were calculated from eq 12 using the values of k_2, $k_3/(k_{-2} + k_9)$, k_2k_9/k_3,and k_5 listed in Table 2B. Supporting electrolyte: 0.1 M CF_3COOH saturated with air. (B) Repeat of (A) but with $[CoP(pyRu(NH_3)_5)_4]^{8+}$ acting as both catalyst and reductant.

When $[CoP(pyRu(NH_3)_5)_4]^{8+}$ instead of $[CoP(pyH)_4]^{4+}$ was employed as the catalyst, the kinetic data shown by the points in Figure 7 were obtained. For this case an additional pathway could become part of the catalytic mechanism: The O_2 molecule in the adduct formed in reaction 2 might be reduced by intramolecular electron transfer as, for example, in reactions 9 and 10. A rate law which allows for the possible occurrence

$$[O_2CoP(pyRu^{II}(NH_3)_5)_4]^{8+} \xrightarrow{k_9}$$

$$[O_2{}^-CoP(pyRu^{II}(NH_3)_5)_3(pyRu^{III}(NH_3)_5)]^{8+} \quad (9)$$

$$[O_2{}^-CoP(pyRu^{II}(NH_3)_5)_3(pyRu^{III}(NH_3)_5)]^{8+} \xrightarrow[H^-]{fast}$$

$$[CoP(pyRu^{II}(NH_3)_5)_2(pyRu^{III}(NH_3)_5)_2]^{10+} + H_2O_2 \quad (10)$$

of reactions 9 and 10 is given in eq 11, where $CoPRu_4$ represents the ruthenated cobalt porphyrin. Integration of eq 11 leads to eq 12 where $b = k_2[CoPRu_4] + k_5(k_{-2} + k_9)/k_3$ and $q =$

$$-\left(\frac{dRu^{II}}{dt}\right) = 2k_2[O_2][CoPRu_4]\left(\frac{k_3[Ru^{II}] + k_9}{k_{-2} + k_9 + k_3[Ru^{II}]}\right) + 2k_5[Ru^{II}][O_2] \quad (11)$$

$$q^{-1/2}\left(\frac{k_{-2} + k_9}{k_3} - \frac{k_2[CoPRu_4]}{k_5}\right) \times$$

$$\ln\left[\frac{(2k_5[Ru^{II}] + b - q^{1/2})(2k_5[Ru^{II}]_0 + b + q^{1/2})}{(2k_5[Ru^{II}] + b + q^{1/2})(2k_5[Ru^{II}]_0 + b - q^{1/2})}\right] +$$

$$\frac{1}{k_5}\ln\left[\frac{\dfrac{k_2k_9[CoPRu_4]}{k_3} + b[Ru^{II}] + k_5[Ru^{II}]^2}{\dfrac{k_2k_9[CoPRu_4]}{k_3} + b[Ru^{II}]_0 + k_5[Ru^{II}]_0{}^2}\right] = -4[O_2]t \quad (12)$$

$(k_2[CoPRu_4] + k_5(k_{-2} + k_9)/k_3)^2 - 4k_2k_5k_9/k_3$. The kinetic data were analyzed in two ways: In the first procedure the data were fit to eq 12 by a nonlinear regression using the known value of k_5 and varying the values of k_2, $(k_{-2} + k_9)/k_3$, and k_2k_9/k_3 to obtain the best agreement with the experimental data. The results of this fitting procedure are shown by the solid lines in Figure 7A. The kinetic data were also analyzed by means of a fitting program, Kinsim, which does not require an analytically

integrated rate law.[20] The mechanism composed of reactions 2−6 plus 9 and 10 was utilized with the known value of k_5, and the values of k_2, k_{-2}, k_3, and k_9 were adjusted to obtain calculated plots of $[Ru^{II}]$ vs time that produced the best match with the experimental data. The best agreement resulted for negligibly small values of k_9 and combinations of the other rate constants which were very similar to those obtained by means of the nonlinear least-squares fit to eq 12. The values of the rate parameters given in Table 2B are the average of the closely similar values obtained from the two data analysis procedures.

Experiments were also conducted using higher concentrations of the $[CoP(pyRu(NH_3)_5)_4]^{8+}$ complex and no other source of Ru(II) so that this complex acted as both the reductant and the catalyst for the reduction of O_2. The kinetic data could still be analyzed on the basis of eqs 11 and 12 and also by Kinsim by making two simplifying assumptions: (i) The concentration of cobalt centers available to participate in reaction 2 was assumed to be constant and equal to the initial concentration of $CoPRu_4$. Thus, the reactions with O_2 of all forms of the catalyst−reductant present, $CoPRu^{II}_4$, $CoPRu^{II}_3Ru^{III}$, ∙∙∙, $CoPRu^{II}Ru^{III}_3$, $CoPRu^{III}_4$, were assumed to be governed by the same rate constants, k_2 and k_{-2}. (ii) All forms of the catalyst−reductant were assumed to reduce the O_2 adduct formed in reaction 2 at the same rate. The second assumption seems reasonable because all of the $Ru^{II}(NH_3)_5py$ centers in $CoPRu_4$ exhibit the same formal potential, independent of the mixture of Ru(II) and Ru-(III) that is present.[2] This pattern means that each Ru center acts independently in electron transfer at electrodes and the same could be assumed to be true in solution. The first assumption is not easy to test, but the values of k_2 that have been reported for a variety of cobalt porphyrins adsorbed on electrodes all lie within an order of magnitude of 10^4 M^{-1} s^{-1}, which suggests that the assumption of constant reactivity toward formation of an O_2 adduct of the $CoPRu_4$ complex as its Ru(II) centers are converted to Ru(III) should not produce major errors. To minimize possible variation, only data collected during the early stages of the reaction, where more than half of the Ru(II) remained unoxidized, were used to obtain the parameters in Table 2B.

The results of the fitting of the experimental data are shown in Figure 7B, and the kinetic parameters obtained are listed in Table 2B. The value of k_2 obtained for the $CoPRu_4$ catalyst is somewhat larger than that for the unruthenated cobalt porphyrin, indicating that the interaction of the Co(II) center of the porphyrin and O_2 is affected by the nature of the cation coordinated to the peripheral pyridine ligands as was assumed

(20) Frieden, C. *Methods Enzymol.* **1994**, *240*, 311.

in previous discussions of the mechanisms by which the porphyrin acts as a catalyst for the electroreduction of O_2.[3] Values of k_2 resulting from kinetic measurements with $CoPRu_4$ adsorbed on graphite electrodes depend on the procedures used for preparing the coatings and the coating thicknesses, but values in the range 10^4-10^5 M^{-1} s^{-1} are typical,[2,3] in approximate agreement with the values in Table 2B.

Discussion

The results presented in this study have shown that in homogeneous solutions the ruthenated cobalt porphyrin, $[CoP-(pyRu(NH_3)_5)_4]^{8+}$, catalyzes only the two-electron reduction of O_2 while it catalyzes the four-electron reduction when adsorbed on graphite electrodes.[2,3] We believe the reason for this contrasting behavior originates in the difference in the rate of electron transfer to the $Co-O_2$ adduct in the two circumstances. When the reduction is carried out in homogeneous solution with one-electron chemical reductants ($Ru(NH_3)_6^{2+}$, $Ru(NH_3)_5py^{2+}$), separate encounters between the reactants are required for the delivery of each electron to the $Co-O_2$ adduct. By contrast, when the adduct is formed by the reaction between O_2 and porphyrin that is adsorbed on the surface of an electrode, multiple electrons can be delivered to the coordinated O_2 molecule at rates that are limited only by the electrode potential. When this rate exceeds the rate of dissociation of the partially reduced dioxygen ligand from the cobalt center of the porphyrin, a four-electron reduction of O_2 is possible. This rationalization could account for the difference in the catalytic behavior of the adsorbed porphyrin following its ruthenation in terms of a slower dissociation of the partially reduced dioxygen ligand from the ruthenated porphyrin.

In the measurements of the stoichiometry of the homogeneous reduction of O_2 when the $CoPRu^{II}_4$ complex served as both catalyst and reductant (Figure 5E), the intermolecular transfer of four electrons from the $CoPRu_4$ reductant to the $O_2-CoPRu_4$ molecule in a single encounter complex was at least conceivable. The result of the experiment in Figure 5E showed that only

two electrons were delivered to each O_2 molecule and separate encounters between reactants could have preceded the transfer of each electron. The reason that the potentially four-electron reductant, $CoPRu^{II}_4$, fails to transfer more than one or two electrons to the $O_2-CoPRu_4$ molecule under conditions, including the thermodynamic driving force, where the four-electron transfer does occur on the electrode surface may be the result of the need to activate two molecules to produce the transition state for the homogeneous electron-transfer reaction but only one molecule when the transfer occurs on the electrode surface.

Perhaps the most interesting result obtained from the kinetic measurements on the chemical reduction of O_2 was the very small value of the rate constant of the possible intramolecular electron transfer step, reaction 9. Both the least-squares fitting of the kinetic data to eq 12 and the use of the Kinsim program to analyze the data led to the conclusion that the contribution of reaction 9 to the kinetics was essentially negligible under the experimental conditions employed. No estimates of the value of k_9 were obtained, but the data indicated that it is no greater than 1 s^{-1} and it could be much smaller. This result is consistent with our previous mechanistic speculation[3] that the Ru centers of the $Ru(NH_3)_5^{2+}$ groups coordinated to the pyridine ligands in $CoPRu_4$ do not cycle between their Ru(II) and Ru-(III) oxidation states as the reduction of O_2 is catalyzed at electrodes on which the $CoPRu_4$ is adsorbed. It is the effect of the coordinated, back-bonding Ru(II) complexes on the interaction between the Co(II) center of the porphyrin and the O_2 molecule coordinated to it that is believed to be the key to the catalytic activity of the $CoPRu_4$ molecules for the four-electron reduction of O_2 at electrodes.

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