charge, size, and basicity between $Fe(CN)_6^{3-}$ and $Ru(CN)_6^{3-}$, we take $\Delta G_5°$ to be very similar for Fe and Ru. Since $E_0 = \Delta G_2° + \Delta G_3° + \Delta G_4° + \Delta G_5°$ and $\Delta G_2°$, $\Delta G_3°$, and $\Delta G_5°$ are the same for Fe and Ru, it follows that the difference in E_0 between Fe and Ru is equal to the difference in the reduction potentials between the $Fe(CN)_6^{3-/4-}$ and $Ru(CN)_6^{3-/4-}$ couples, as observed experimentally.

Although the spectral characteristics of II discussed above support a trapped-valence formulation featuring Ru(III) and Fe(II), some delocalization obtains. The extent of delocalization can be assessed from a calculation of the parameters α^2 and H_{AB}, eq 11-13. Taking $\bar{\nu}_{max} = 1.02 \times 10^4$ cm^{-1}, $d = 5.2$ Å (distance

$$\alpha^2 = 4.24 \times 10^{-4}\epsilon_{max}(\Delta\bar{\nu}_{1/2})/\bar{\nu}_{max}d^2 \qquad (11)$$

$$H_{AB} = \bar{\nu}_{max}\alpha \qquad (12)$$

$$\Delta\bar{\nu}_{1/2} = (2310\bar{\nu}_{max})^{1/2} \qquad (13)$$

between metal centers), and $\epsilon_{max} = 3.0 \times 10^3$ M^{-1} cm^{-1}, we calculate $\Delta\bar{\nu}_{1/2} = 4.9 \times 10^3$ cm^{-1}, $\alpha^2 = 2.2 \times 10^{-2}$, and $H_{AB} = 1.5 \times 10^3$ cm^{-1} from eq 11-13. Results of similar calculations for analogous cyano-bridged binuclear complexes are presented in Table II. The small values of the delocalization parameter ($\alpha^2 \sim 2\%$) in all cases support the trapped valence description for the compounds. The extent of electronic coupling for cyano-bridged complexes is considerably higher ($H_{AB} = (1-2) \times 10^3$ cm^{-1}) than values found for pyrazine-bridged complexes ($H_{AB} = (3-5) \times 10^2$ cm^{-1}).[33,36] Such a trend was noted before[37] and can reasonably be ascribed, if the coupling between sites is dominated by metal centers–bridging ligand mixing,[38] to a shorter bridge in CN^- and to the availability of a pair of perpendicular π^* orbitals on the bridging ligand. Alternatively, direct πd–πd overlap may play a role in delocalization when the bridging ligand is cyanide.

Registry No. $Ru(NH_3)_5OH_2^{3+}$, 25590-52-7; $Fe(CN)_6^{4-}$, 13408-63-4.

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Contribution from the Edison Biological Laboratory,
Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254

Oxidative Chemistry of Nickel Hydroporphyrins

Alan M. Stolzenberg* and Matthew T. Stershic

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The chemical and electrochemical oxidations of nickel porphyrin, chlorin, and isobacteriochlorin complexes in the octaethyl and methyl-substituted octaethyl series were investigated in nonaqueous media. The potentials for oxidation of the complexes were determined by cyclic voltammetry in acetonitrile, methylene chloride, and dimethylformamide solutions containing TBAP as supporting electrolyte. EPR and absorption spectroscopy were used to characterize the one- and two-electron-oxidized complexes. The first oxidation of all complexes yielded nickel(II) cation radicals. Unlike $Ni(TPP)^{\bullet+}$, the cation radical complexes did not undergo internal electron transfer to afford nickel(III) complexes at low temperatures. Nickel(II) dication complexes were the product of the second oxidation of nickel porphyrins and chlorins in acetonitrile. The second oxidation of nickel isobacteriochlorins afforded nickel(III) cation radical complexes. The results suggest that the greatly enhanced stability of oxidized *cis*-Ni(OEC) species is not a consequence of redox activity of the coordinated nickel but rather of the ruffled conformation of the macrocycle.

Recently, we reported a remarkable increase in the stability of oxidized *cis*-octaethylchlorin species when coordinated to nickel.[1] Dications of β-hydrogenated hydroporphyrins,[2] of which chlorins are a subgroup, typically undergo partial dehydrogenation on the cyclic voltammetric time scale to afford more extensively unsaturated macrocycles.[3] The compounds formed upon oxidation of free-base *cis*-H_2(OEC)[4] were considerably less stable. On the same time scale, dehydrogenation of *cis*-$H_2(OEC)^{2+}$ was complete and that of *cis*-$H_2(OEC)^{\bullet+}$ was extensive.[1,5] Metalation of *cis*-OEC with Cu(II), Mg(II), Sn(IV), or Zn(II) increased the stability of the cation radical somewhat, but formation of the cation radical was reversible only for the Mg complex. The second oxidations of all four complexes remained totally irreversible. In contrast, both oxidations of *cis*-Ni(OEC) were reversible on the cyclic voltammetric time scale (100 mV/s sweep rate).

Nickel hydroporphyrin complexes differ substantially from free-base and other metallohydroporphyrin complexes in one important respect that may enhance the stability of *cis*-$Ni(OEC)^{\bullet+}$. X-ray structural studies show that the macrocycle in nickel hydroporphyrin complexes invariably experiences a marked S_4 ruffle and is saddle-shaped.[6,7] Ruffling is a consequence of both the flexibility of hydroporphyrins[1,6b,7c,8] and the mismatch of the metal–nitrogen bond lengths optimal for square-planar, low-spin nickel(II) and for planar porphyrin or hydroporphyrin macrocycles.[6b,7c] The conformations of Ni(OEC) complexes are also ruffled in solution.[1] The OEC macrocycle must therefore flatten out to form Ni(OEP) by dehydrogenation of the *cis*-Ni(OEC) dication. A comparable conformational change is not required for the dehydrogenation of the other *cis*-OEC complexes. Because ruffling of nickel hydroporphyrins is a spontaneous process, flattening the macrocycle provides an endergonic contribution to

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(4) Abbreviations: OEP, 2,3,7,8,12,13,17,18-octaethylporphyrin dianion; OEC, 2,3-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrin dianion (chlorin); OEiBC, mixture of *ttt*- and *tct*-2,3,7,8-tetrahydro-2,3,7,8,12,13,17,18-octaethylporphyrin dianion (isobacteriochlorin); MOEC, 2,3-dihydro-2-methyl-3,3,7,8,12,13,17,18-octaethylporphyrin dianion; DMOEiBC, mixture of *syn*- and *anti*-2,7-dihydro-2,7-dimethyl-3,3,8,8,12,13,17,18-octaethylporphyrin dianion; TPP, 5,10,15,20-tetraphenylporphyrin dianion; TPC, 2,3-dihydro-5,10,15,20-tetraphenylporphyrin dianion; TPiBC, 2,3,7,8-tetrahydro-5,10,15,20-tetraphenylporphyrin dianion; DMF, *N,N*-dimethylformamide; TEAP, tetraethylammonium perchlorate; TBAP, tetra-*n*-butylammonium perchlorate; TBAH, tetra-*n*-butylammonium hexafluorophosphate.

(5) Dehydrogenation of the cation radical can occur via the thermodynamically unfavorable disproportionation to the dication, provided that the latter reacts irreversibly and rapidly. $H_2(OEiBC)^{\bullet+}$ dehydrogenates in this manner, albeit more slowly.[3]

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both the activation energy and overall free energy change for dehydrogenation of *cis*-Ni(OEC) dication. This would explain the enhanced stability of the nickel complex and would represent one of the first examples of the conformation of the macrocycle significantly affecting the chemical reactivity of a metallotetrapyrrole.

The stability of oxidized *cis*-Ni(OEC) complexes could also be rationalized in an altogether different fashion: one of the oxidations could be metal centered. Several groups have presented evidence for the accessibility of Ni(III) in a porphyrin environment. Wolberg and Manassen investigated the electrochemical oxidation of Ni(TPP) in 0.1 M TBAP–benzonitrile.[9] Although EPR silent at room temperature, the oxidized complex had a spectrum characteristic of $\mathrm{Ni^{III}(TPP)^{+}}$ at liquid-nitrogen temperature. Dolphin and co-workers examined the oxidation of Ni(TPP) in methylene chloride in the presence of either TBAP, TBAH, or $\mathrm{Br^-}$.[10] One-electron oxidation at room temperature afforded a green solution whose UV–vis and EPR spectra were characteristic of $\mathrm{Ni^{II}(TPP)^{\bullet+}}$. An orange-red solid was obtained when the green solutions containing TBAP or TBAH were frozen at 77 K. EPR and optical spectra of the solid suggested that an internal electron transfer had occurred to yield $\mathrm{Ni^{III}(TPP)^{+}}$. (This change did not occur in the presence of $\mathrm{Br^-}$ or of small amounts of water.) Resonance Raman data presented by Spiro provided further evidence for the change in the site of oxidation upon freezing.[11] Kadish investigated the oxidations of several nickel(II) porphyrins in a number of solvents and electrolytes.[12] Three different mechanisms were found to occur. The first was consistent with Dolphin's observations. $\mathrm{Ni^{III}(P)^{+}}$ was obtained upon freezing the initial one-electron oxidation product, $\mathrm{Ni^{II}(P)^{\bullet+}}$. Further oxidation of $\mathrm{Ni^{II}(P)^{\bullet+}}$ yielded the dication $\mathrm{Ni(P)^{2+}}$. In the second mechanism, the initial product was the cation radical $\mathrm{Ni^{II}(P)^{\bullet+}}$. Cooling to 77 K did not induce internal electron transfer. The second oxidation yielded the nickel(III) cation radical $\mathrm{Ni^{III}(P)^{\bullet 2+}}$. Nickel(III) was inaccessible in the third mechanism. Clearly, the site of oxidation is determined by a considerable number of factors including the substituents, solvent, electrolyte, temperature, and oxidant. It is equally clear that the nickel ion and the porphyrin π-system can be oxidized at comparable potentials.

There have been few detailed investigations of the oxidations of nickel porphyrin complexes (other than tetraaryl substituted) or nickel chlorin complexes. Oxidation of Ni(OEP) afforded the cation radical $\mathrm{Ni(OEP)^{\bullet+}}$.[10,13,14] The site of oxidation was reported to remain the same upon freezing.[10] Potentials for the first oxidation of chlorins shift 0.2–0.3 V negative of the corresponding porphyrin oxidation.[3,12,15,16] As expected, oxidation of Ni(TMC)[12] and *trans*-Ni(OEC)[15] resulted in nickel(II) cation radicals. Further oxidation of $\mathrm{Ni(TMC)^{\bullet+}}$ afforded the dication $\mathrm{Ni(TMC)^{2+}}$.

Our interest in the conformations of nickel hydroporphyrin complexes[1] and the effect of conformation on reactivity have led us to investigate the redox reactions of nickel complexes of β-alkyl-substituted porphyrins and hydroporphyrins. In this paper we examine the electrochemistry of complexes in the octaethyl and methylated octaethyl series and characterize the oxidation products of these complexes by use of UV–vis spectroscopy, spectroelectrochemistry, and EPR spectroscopy. Our results suggest that the enhanced stability of oxidized *cis*-Ni(OEC) does not arise from formation of a nickel(III) complex. Details of the reductive chemistry of nickel hydroporphyrins are presented elsewhere.[17]

Experimental Section

Materials. Acetonitrile (HPLC grade) and methylene chloride were distilled from calcium hydride. DMF (Burdick and Jackson distilled in glass) was dried and stored over activated 4A sieves. Polarographic grade tetrabutylammonium perchlorate was used as obtained from Eastman Kodak Co. All other reagents and solvents were reagent or HPLC grade and were thoroughly degassed prior to use.

Preparation of Complexes. $\mathrm{H_2(OEP)}$,[18] Ni(OEP),[19] *trans*-$\mathrm{H_2(OEC)}$[20] (hereafter referred to as simply OEC), Ni(OEC),[1] $\mathrm{H_2(OEiBC)}$,[3] Ni(OEiBC),[17] $\mathrm{H_2(MOEC)}$,[21] Ni(MOEC),[17b] $\mathrm{H_2(DMOEiBC)}$,[21] and Ni(DMOEiBC)[17b] were prepared by literature methods. The quantity of DMOEiBC compounds that was available was extremely limited owing to the difficulty of access to the oxoporphyrin starting material and the low yields of the synthetic procedure. Because *cis*- and *trans*-Ni(OEC) are oxidized at comparable potentials,[1] we confined our investigations to the much more readily available trans isomer of Ni(OEC). The description of the oxidized complexes is likely to be the same for the two isomeric nickel chlorin complexes.

Amminium Salts. $[(p\text{-BrC}_6\text{H}_4)_3\text{N}][\text{SbCl}_6]$. $(p\text{-BrC}_6\text{H}_4)_3\text{N}$ was prepared by bromination of triphenylamine.[22] The crude product was purified by recrystallization from methanol. The quantitative absorption spectrum of the amine was determined to permit correction of the spectra of oxidized complexes prepared by use of its amminium salt. UV–vis ($\mathrm{CH_2Cl_2}$) λ_{max}, nm ($10^{-3}\,\epsilon_M$, $\mathrm{cm^{-1}}$): 216 (35.8), 308 (31.7). The amminium salt (the term amminium is used to represent the cation radical of the corresponding amine) was prepared by reaction of the amine with $\mathrm{SbCl_5}$ in methylene chloride.[23] The quantitative absorption spectrum of the amminium salt was determined with dilute solutions to ensure that dissolution was complete. Solutions of the salt are intensely colored (opaque) and are saturated at concentrations less than 10 mM. UV–vis ($\mathrm{CH_2Cl_2}$) λ_{max}, nm ($10^{-3}\epsilon_M$, $\mathrm{cm^{-1}}$): 211 (51.7), 276 (12.9), 368 (19.5), 729 (33.9). The extinctions are about 5% higher than previously reported.[23]

$[(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{N}][\text{SbCl}_6]$. Tri-*p*-tolylamine was purchased from Specialty Organics, Inc., Irwindale, CA. UV–vis ($\mathrm{CH_2Cl_2}$) λ_{max}, nm ($10^{-3}\epsilon_M$, $\mathrm{cm^{-1}}$): 216 (29.8), 302 (24.4). The amminium salt was prepared as above. UV–vis ($\mathrm{CH_2Cl_2}$) λ_{max}, nm ($10^{-3}\epsilon_M$, $\mathrm{cm^{-1}}$): 210 (54.5), 276 (15.0), 348 (19.0), 358 (19.2), 369 (21.8), 676 (28.4).

Physical Measurements. Critical manipulations and measurements were carried out under a nitrogen or argon atmosphere owing to the air sensitivity of the majority of the compounds. Absorption spectra were recorded on a Perkin-Elmer Lambda 4C spectrophotometer. Spectral subtractions were performed with the attached 7000 Series computer. EPR spectra were determined on a Varian E-6 spectrometer. Samples were either at room temperature or frozen at 100 K.

Cyclic voltammetric measurements were made under an argon atmosphere in a conventional three-electrode cell. Solutions were 0.1 M in TBAP. The working electrode was a platinum disk, and a platinum wire served as the counter electrode. A saturated calomel electrode (SCE) was separated from the bulk solution by a porous Vycor disk. Potentials are reported both relative to the SCE and to the ferrocenium/ferrocene couple of ferrocene added to the test solution. The instrumentation used included a Princeton Applied Research Model 173 potentiostat–galvanostat, a Model 176 current to voltage converter, and a Model 175 universal programmer. Data were recorded on a Bascom-Turner Model 3120T digital recorder. The digitization rate was sufficient to record data points at intervals of 2 mV or less.

Spectroelectrochemical experiments were conducted in the sample compartment of the Lambda 4C spectrophotometer by using an optically transparent thin-layer electrode cell (OTTLE). The OTTLE was of a gold minigrid (200 lines/in.)–quartz microscope slide variety and has been described previously.[3] A miniature sodium chloride saturated calomel electrode (−7 mV vs SCE) was used as the reference electrode.

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Table I. Potentials of the Oxidations of Free-Base and Nickel(II) Porphyrin and Hydroporphyrin Complexes in Selected Solvents

		$E_{1/2}$,[a,b] V				
		1+/0		2+/1+		other
complex	solvent	vs SCE	vs Fc^+/Fc[c]	vs SCE	vs Fc^+/Fc[c]	vs SCE
H_2(OEP)	*n*-PrCN[d]	0.89		1.40[e]		
	DMF	0.96[f]	0.46	1.19[e,g]	0.69	1.30[e]
H_2(OEC)	CH_3CN	0.59	0.19	1.11	0.70	
	DMF	0.70	0.20	1.23[e,h]	0.73	1.70[e]
H_2(OEiBC)	CH_3CN	0.34	−0.07	0.88	0.47	
H_2(MOEC)	CH_2Cl_2	0.58	0.13	1.22[e]	0.77	
	CH_3CN	0.59	0.19	1.17[e]	0.76	
	DMF	0.71[f]	0.21	1.12[e,g]	0.62	
H_2(DMOEiBC)	CH_2Cl_2	0.33	−0.12	1.02[e]	0.57	
	CH_3CN	0.34	−0.07	0.93[e]	0.52	
	DMF	0.46	−0.04	0.88[e,h]	0.38	
Ni(OEP)	CH_2Cl_2	0.77	0.32	1.24	0.79	
	C_6H_5CN[i]	0.73				
Ni(OEC)	CH_2Cl_2	0.48	0.03	1.03	0.58	1.8,[e,h] 1.9[e]
	CH_3CN	0.48	0.07	0.82	0.41	
	DMF	0.59	0.09	0.83[e]	0.33	0.91,[e] 1.05[e]
Ni(OEiBC)	CH_2Cl_2	0.21	−0.24	0.86	0.41	
	CH_3CN	0.22	−0.19	0.61	0.21	
	DMF	0.30	−0.20	0.62[e,h]	0.12	0.85,[e] 0.92[e], 1.06[e]
Ni(MOEC)	CH_2Cl_2	0.48	0.04	1.07[f]	0.62	1.52[e,h]
	CH_3CN	0.48	0.07	0.83[f]	0.42	
	DMF	0.59	0.09	0.83[e]	0.33	1.20[e,h]
Ni(DMOEiBC)	CH_2Cl_2	0.23	−0.22	0.96[e]	0.51	
	CH_3CN	0.20	−0.20	0.67[e]	0.26	1.66[e,h]
	DMF	0.32	−0.18	0.57[e]	0.07	1.0,[e,g] 1.2[e]

[a] $E_{1/2} = {}^1/_2(E_{p,a} + E_{p,c})$. [b] At 25 °C in a solution 0.1 M in TBAP with a Pt-disk working electrode and 100 mV/s scan rate. [c] Ferrocene was added to the test solution at the conclusion of the experiment. [d] Reference 3. [e] $E_{p,a}$ (irreversible). [f] $i_{p,c} < i_{p,a}$. [g] Anodic current equivalent to more than two electrons. [h] Two-electron process. [i] Reference 28.

The OTTLE cell was loaded in an inert-atmosphere drybox immediately prior to the experiment. Spectra of complexes in the OTTLE cell were recorded vs air and were corrected by subtraction of the spectrum of the OTTLE cell filled with the appropriate solvent.

Spectrophotometric titrations of the nickel complexes with amminium salts or bromine were carried out in cells fitted with rubber septa. Oxidant was added by microliter syringe. Concentrations of complex and oxidant, cell path lengths, and solution volumes were chosen to minimize dilution during the titration. Typically, solutions of the nickel complexes were 10^{-5} M and those of oxidant were 10^{-3} M. The actual concentrations of the amminium salt solutions were checked spectrophotometrically. UV-vis spectra of the nickel complex recorded after each addition of amminium salt were corrected by subtracting the absorption that would result from the concentration of triarylamine calculated to be in solution (assuming complete conversion of amminium to amine). When the corrected spectra of Ni(OEP) or Ni(OEC) were overlayed, isosbestic points were present.

Results

Voltammetry. The oxidations of free-base and nickel porphyrin and hydroporphyrin complexes in the octaethyl and methylated octaethyl series were investigated by use of cyclic voltammetry. Oxidations were examined in CH_3CN, CH_2Cl_2, and dimethylformamide (DMF). The limited solubility of Ni(OEP) in CH_3CN and DMF precluded experiments in these solvents. Potentials vs SCE and the ferrocenium/ferrocene couple are reported in Table I. Some literature data for complexes are included for purposes of comparison.

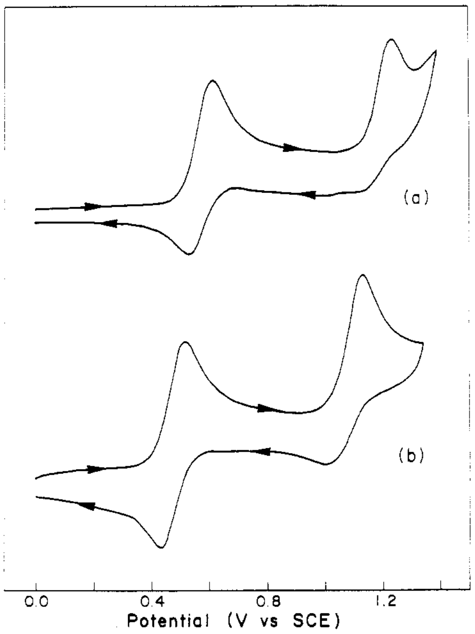

Figure 1. Cyclic voltammograms of the 1+/0 and 2+/1+ processes of (a) H_2(MOEC) and (b) Ni(MOEC) recorded at 100 mV/s in methylene chloride solution 0.1 M in TBAP.

The electrochemical behavior of the complexes in CH_3CN and CH_2Cl_2 solution was typical for the most part of porphyrin and hydroporphyrin complexes.[1,3,12,16,24-26] Two one-electron oxidations were observed. Half-wave potentials of the first oxidations shifted negatively by 250–300 mV for each increase in the saturation level of the macrocycle. The first oxidations were reversible. Free-base compounds in the octaethyl series had irreversible second oxidations ($i_{p,c}$ slightly less than $i_{p,a}$), but those of the corresponding nickel complexes were reversible. In contrast, all second oxidations in the methylated octaethyl series were markedly irreversible. The cyclic voltammogram of the representative compound H_2(MOEC), Figure 1a, illustrates that a cathodic peak corresponding to the rereduction of the doubly oxidized species was absent. Only Ni(MOEC) had a well-defined cathodic peak, Figure 1b. The lesser stability of doubly oxidized complexes in this series relative to hydrogenated hydroporphyrins is noteworthy. It contrasts with the reported exceptional stability of the singly oxidized complex $H_2(DMOEiBC)^{\bullet+}$ relative to $H_2(OEiBC)^{\bullet+}$.[21] Given the insta-

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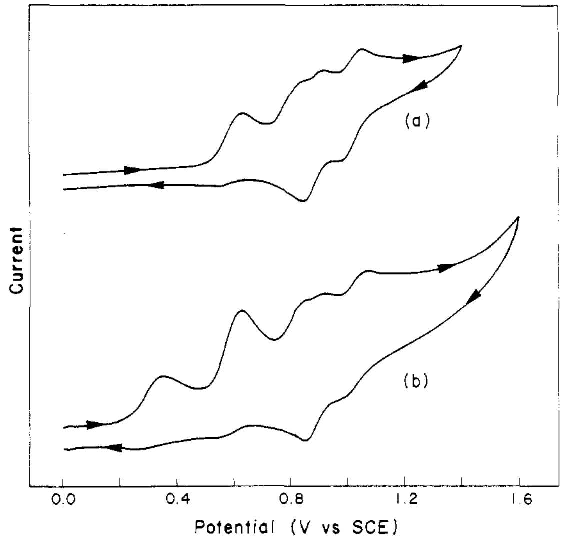

Figure 2. Cyclic voltammograms of the oxidative processes of (a) Ni(OEC) and (b) Ni(OEiBC) recorded at 100 mV/s in DMF solution 0.1 M in TBAP.

bility of the methylated octaethylhydroporphyrins in these experiments and our limited supply of these complexes, we did not attempt to prepare and characterize bulk samples of the oxidized complexes of this series.

The behavior of the complexes changed significantly in DMF solution. The first oxidation of Ni(OEC) was reversible if scanned separately. Instead of the reversible, one-electron second oxidation that had been observed in the other solvents, the voltammogram of Ni(OEC), Figure 2a, exhibited two overlapping anodic peaks at 0.83 and 0.91 V vs SCE. A fourth anodic peak was found at 1.05 V. The irreversibility of these processes was apparent from the absence of corresponding cathodic peaks. However, at slow scan rates or upon repetitive cycling between 0.70 and 1.20 V, a cathodic peak at 0.84 V increased in prominence. Concurrently, the anodic peak at 0.83 V decreased and that at 0.91 V increased. These changes are consistent with a reaction of DMF (or an impurity therein) with the chlorin dication, $Ni(OEC)^{2+}$. The voltammograms of $H_2(OEP)$ and $H_2(OEC)$ also demonstrated that tetrapyrrole dications are unstable in DMF. A likely possibility for the reaction with hydroporphyrin complexes is that DMF promotes oxidative dehydrogenation[3] to more extensively unsaturated macrocycles, for example Ni(OEC) to Ni(OEP). Unfortunately, the limited solubility of Ni(OEP) in DMF precluded confirmation that the anodic peak at 0.91 V in the voltammogram of Ni(OEC) was a Ni(OEP) oxidation. Anodic peaks were observed in the voltammogram of Ni(OEiBC), Figure 2b, at potentials corresponding to Ni(OEC) processes, however. Alternatively, addition of DMF to the dication may yield an isoporphyrin analogue, which can undergo oxidation.[27]

Two relationships of potentials, $\Delta_{ox} = E_{1/2}^{ox}(2) - E_{1/2}^{ox}(1) = 0.3 \pm 0.1$ V and $\delta = E_{1/2}^{ox}(1) - E_{1/2}^{red}(1) = 2.25 \pm 0.15$ V, have been determined for many M(OEP) complexes and serve as criteria for ligand-based oxidation and reduction.[16,28,29] Similar criteria for M(OEC) and M(OEiBC) complexes are not useful here. The δ type criterion is inapplicable because the first reduction of Ni(OEC) and Ni(OEiBC) is metal centered.[17] Insufficient data is available to determine the Δ_{ox} parameter for these complexes with a reasonable degree of confidence.[1,3] One potentially useful criterion for the site of oxidation exists, however. The 250–300-mV negative shift of the first oxidation potential observed for each increase in the saturation level of free-base hydroporphyrins is preserved in the analogous metallohydroporphyrin series when the metal is not redox active.[1,3,12,24,25]

Table II. Quantitative Absorption Spectral Data for Ni(P) Cations[a]

complex	λ_{max}, nm (ϵ,[b] mM)
$Ni^{II}(OEP)^{+}$ [c]	375 (102), 500 (8.1), 575 (6.5)
$Ni^{II}(OEP)^{2+}$ [c]	330 (65.2)
$Ni^{II}(OEC)^{+}$	366 (49.3), 386 (47.6), 548 (3.7), 658 (3.7)
$Ni^{II}(OEC)^{2+}$	334 (43.1)
$Ni^{II}(OEiBC)^{+}$	316 (12.2), 359 (35.4), 377 (44.5), 391 (45.9), 510 (5.1), 586 (3.0), 640 (4.2)
$Ni^{III}(OEiBC)^{\bullet 2+}$	356 (53.0), 374 (sh, 47.6), 386 (sh, 36.7), 643 (2.9)

[a] Acetonitrile solution, 0.1 M in TBAP. [b] Relative precision of extinction coefficients is as indicated; determination of extinction coefficients is accurate only to several percent. [c] Methylene chloride solution, 0.1 M in TBAP.

The most important solvent effect noted was on the potentials of the oxidation processes. Ferrocene was used as an internal reference in order to eliminate the contribution of junction potentials to potentials measured in the different solvents. It is evident from the data reported relative to Fc^+/Fc that the potential of the first oxidations of the complexes are independent of the identity of the solvent. Furthermore, the 250–300-mV negative shift in the potential of the first oxidation with each increase in saturation of the macrocycle is preserved in the nickel complexes. Both results strongly imply that the first oxidations of the nickel complexes are macrocycle centered; i.e., they yield nickel(II) cation radicals. Interestingly, unlike those for nickel porphyrin complexes,[12] the potential of the second oxidation of the nickel hydroporphyrin complexes was solvent dependent. In general, the potential of this oxidation became more negative in the more polar and more strongly coordinating solvents. Particularly noteworthy were the 300–400-mV shifts observed for this oxidation process in Ni(OEiBC) and Ni(DMOEiBC) as the solvent was changed from CH_2Cl_2 to DMF. Shifts in the potentials of nickel chlorin complexes were somewhat less pronounced. The solvent dependence of potential is suggestive of stabilization of a nickel(III) member of a redox couple by stronger solvent ligation. Consistent with this, addition of a small excess of piperidine (10 mM) to Ni(OEiBC) in CH_2Cl_2 resulted in a 250–300-mV negative shift in the potential of the second oxidation, but little change in the potential of the first oxidation. Thus, the voltammetric data imply that the product of the second oxidation of nickel isobacteriochlorin complexes and perhaps of nickel chlorin complexes could be a nickel(III) cation radical rather than a nickel(II) dication.

Oxidation of Nickel Complexes. Spectroelectrochemistry. In order to provide spectral characterization of electrochemically generated oxidized species, the first and second oxidation products of Ni(OEP), Ni(OEC), and Ni(OEiBC) were examined spectroelectrochemically by use of an OTTLE cell. Experiments with each complex are described below. Spectral data for oxidized species are present in Table II.

(a) Ni(OEP). The electrolysis of Ni(OEP) was examined in butyronitrile and in CH_2Cl_2 solution. The experiments in CH_2Cl_2 are described first. Spectra obtained in this solvent are presented in Figure 3.

Oxidation of Ni(OEP) at 0.95 V led to the loss of the visible bands at 515 and 551 nm. These were replaced by weak, extremely broad bands at 500 and 575 nm. The Soret band at 390 shifted to 375 nm and decreased in intensity by roughly a factor of 2. The final spectrum agreed well with the previously reported spectra of $Ni(OEP)^{\bullet +}$.[13,14] Reduction of $Ni(OEP)^{\bullet +}$ at 0.0 V after 10 min at 0.95 V led to quantitative recovery of the Ni(OEP) spectrum. No changes in the spectra described above were noted after several oxidation–reduction cycles.

The two-electron-oxidized complex was generated by electrolysis of Ni(OEP) at 1.90 V. Formation of this complex proceeded via the intermediacy of $Ni(OEP)^{\bullet +}$. The complex had a rather featureless spectrum with a single broad peak at 330 nm. The absorbance was essentially negligible at wavelengths longer than 450 nm. The spectrum was consistent with formation of a me-

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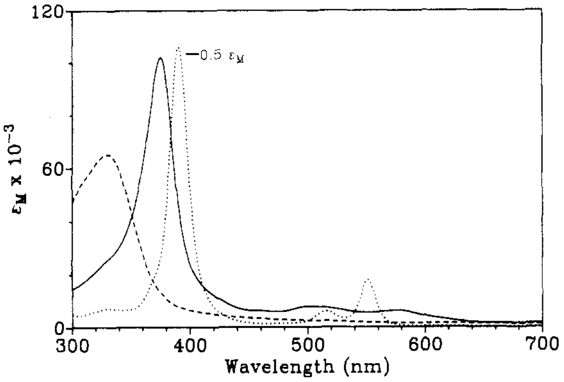

Figure 3. UV-vis spectra of Ni(OEP) (···), Ni(OEP)$^{\bullet+}$ (—), and Ni(OEP)$^{2+}$ (- -) in methylene chloride containing 0.1 M TBAP recorded in the OTTLE cell. Ni(OEP)$^{\bullet+}$ and Ni(OEP)$^{2+}$ were produced by electrolysis at 0.95 and 1.90 V vs SSCE, respectively. For convenience, the scale of the Ni(OEP) spectrum was reduced by half. Actual extinctions for Ni(OEP) are twice those shown in the figure.

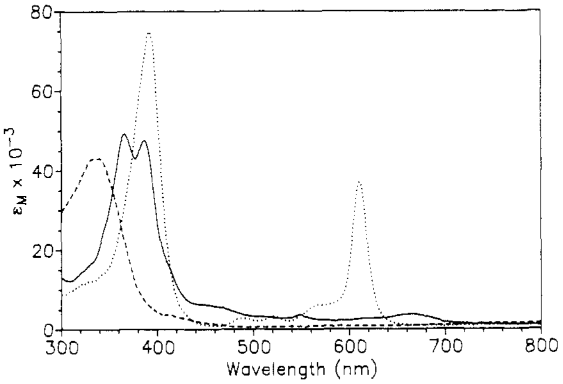

Figure 4. UV-vis spectra of Ni(OEC) (···), Ni(OEC)$^{\bullet+}$ (—), and Ni(OEC)$^{2+}$ (- -) in acetonitrile containing 0.1 M TBAP recorded in the OTTLE cell. Ni(OEC)$^{\bullet+}$ and Ni(OEC)$^{2+}$ were produced by electrolysis at 0.65 and 0.95 V vs SSCE, respectively.

talloporphyrin dication.[29] Reduction of 0.0 V after 6–10 min at 1.90 V resulted initially in recovery of the Ni(OEP)$^{\bullet+}$ spectrum followed by quantitative recovery of the Ni(OEP) spectrum. Several oxidation–reduction cycles of comparable duration were performed without spectral degradations.

The results obtained in butyronitrile were similar to those above with one exception: the spectrum of the product of electrolysis at 0.95 V was different. The Soret band in butyronitrile was appreciably broader and less intense. It had a maximum at 353 nm and a shoulder at 375 nm. Also observed were a weak broad band at 525 nm and one side of an extremely broad band that had a maximum at wavelengths greater than 900 nm. The spectrum of oxidized Ni(OEP) in butyronitrile closely resembled those of the dimeric cation radicals [M(OEP)$^{\bullet}$]$_2^{2+}$, where M = Zn and Mg.[29,30] [Ni(OEP)$^{\bullet}$][SbCl$_6$] is dimeric in the solid state.[14]

(b) Ni(OEC). The UV-vis spectra of Ni(OEC) and its oxidation products in CH$_3$CN are presented in Figure 4. Electrolysis at 0.65 V led to a final spectrum that was consistent with formation of the Ni(OEC)$^{\bullet+}$ cation radical. The prominent visible band of Ni(OEC) at 614 nm was replaced by broad, weak bands at 548 and 659 nm. As in the case of Ni(OEP), the Soret band of Ni(OEC) blue-shifted and diminished in intensity upon oxidation. It also split into two overlapping peaks at 366 and 386 nm. The spectrum was similar to that reported for Ni(OEC)$^{\bullet+}$ (in 4:1 CHCl$_3$/CH$_3$OH) obtained by oxidation of Ni(OEC) with ferric perchlorate,[15] but reported extinctions were somewhat greater.[31]

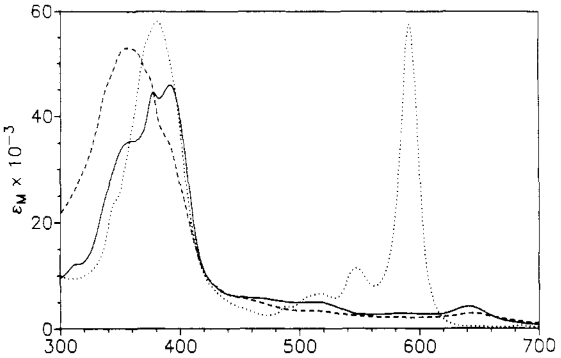

Figure 5. UV-vis spectra of Ni(OEiBC) (···), Ni(OEiBC)$^{\bullet+}$ (—), and Ni^{III}(OEiBC)$^{\bullet 2+}$ (- -) in acetonitrile containing 0.1 M TBAP recorded in the OTTLE cell. Ni(OEiBC)$^{\bullet+}$ and Ni^{III}(OEiBC)$^{\bullet 2+}$ were produced by electrolysis at 0.40 and 0.70 V vs SSCE, respectively.

Reduction at 0.0 V gave complete recovery of Ni(OEC).

Electrolysis at 0.95 V led after initial formation of Ni(OEC)$^{\bullet+}$ to formation of a complex with a UV-vis spectrum similar to that of Ni(OEP)$^{2+}$. The single broad peak observed at 339 nm and the minimal absorption above 450 nm suggested formation of Ni(OEC)$^{2+}$. Reduction at 0.0 V after 5 min at 0.95 V first led to recovery of the Ni(OEC)$^{\bullet+}$ spectrum and then resulted in nearly complete recovery of the Ni(OEC) spectrum. Repeated oxidation–reduction cycles (0.95 V) led to partial conversion (5%) of Ni(OEC) to Ni(OEP).

(c) Ni(OEiBC). Electrolysis of Ni(OEiBC) in CH$_3$CN at 0.40 V led to changes in the UV-vis spectrum, Figure 5, that were analogous to those observed upon formation of Ni(OEC)$^{\bullet+}$. The spectrum of Ni(OEiBC)$^{\bullet+}$ consisted of two broad, weak bands at 518 and 641 nm and a Soret band with features at 360 (sh), 380, and 392 nm. The intensity of the Soret band was only slightly less than that of neutral Ni(OEiBC). The recovery of Ni(OEiBC) upon reduction of the cation radical at 0.0 V was less than complete. After several oxidation reduction cycles, conversion of Ni(OEiBC) to Ni(OEC) was about 10% as judged by the Ni(OEC) peak at 614 nm.

The final spectrum obtained during electrolysis of Ni(OEiBC) at 0.70 V differed significantly from the spectra of the Ni(OEP)$^{2+}$ and Ni(OEC)$^{2+}$ dications. Although blue-shifted relative to Ni(OEiBC)$^{\bullet+}$, the Soret bands of the doubly oxidized species occurred at significantly longer wavelengths than the Soret band of either of the above dications. Absorption at wavelengths greater than 400 nm was not negligible. Instead, extinctions and band shapes were comparable to those of the cation radical, Ni(OEiBC)$^{\bullet+}$. The results suggest that the second oxidation occurred at nickel to afford Ni^{III}(OEiBC)$^{\bullet 2+}$. Additional support for this assignment is provided by the substantial differences between the spectrum of the nickel complex and the spectrum of Zn(OEiBC)$^{2+}$.[3] (The spectrum of the latter was rather featureless with broad weak bands at 347 and 373 nm.) The spectra should have been similar if substitution of Ni(II) for Zn(II) was the only difference between the complexes. Reduction of Ni^{III}(OEiBC)$^{\bullet 2+}$ at 0.00 V led to initial recovery of the Ni(OEiBC)$^{\bullet+}$ spectrum followed by subsequent recovery of the spectrum of Ni(OEiBC). As in the case of the first oxidation, repeated oxidation and reduction cycles resulted in about 10% conversion of Ni(OEiBC) to Ni(OEC). In contrast to this result, neither Zn(OEiBC)$^{\bullet+}$ nor Zn(OEiBC) were recovered upon reduction of Zn(OEiBC)$^{2+}$.[3]

Chemical Oxidation. Electrochemical oxidations are by necessity conducted in media of moderately high ionic strength (0.1 M electrolyte). Chemical oxidations, on the other hand, can be performed in media of low ionic strength. Because the site of oxidation of Ni(TPP) is sensitive to the solvent medium, the oxidant, and the counterion, we investigated the reactions of the nickel complexes with chemical oxidants.

Three chemical oxidants were used: tri-*p*-tolylamminium hexachloroantimonate, tris(*p*-bromophenyl)amminium hexachloroantimonate, and bromine. Bromine may react with por-

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(31) Extinctions reported for *trans*-Ni(OEC) in ref 15 are higher by roughly the same factor than the values that we reported in ref 1. Note also that spectra were recorded in different solvent media.

phyrin or hydroporphyrin complexes by mechanisms other than simple outer-sphere electron transfer. Its byproduct, bromide, could potentially interact with the oxidized complexes. In contrast, the two tri-para-substituted triphenylamminium hexachloroantimonate salts, which function as one-electron oxidants, have byproducts that are nonnucleophilic. The para substituents control the reduction potential of the amminium radical cation. The tri-*p*-tolylamminium salt is the weaker oxidant of the two and has $E_{1/2} = 0.75$ V (vs SCE) in CH_3CN.[32] It is a sufficiently strong oxidant to effect the first oxidation of Ni(OEC) and Ni(OEiBC) but probably should not effect the second oxidation of these complexes. The tris(*p*-bromophenyl)amminium salt, with $E_{1/2} = 1.05$ V,[32] can effect the first oxidations of Ni(OEP), Ni(OEC), and Ni(OEiBC) as well as the second oxidations of the latter two complexes.

Solutions of Ni(OEP), Ni(OEC), and Ni(OEiBC) in methylene chloride were titrated with either a stoichiometric amount of amminium salt [tris(*p*–bromophenyl)amminium for Ni(OEP), tri-*p*-tolylamminium for Ni(OEC) and Ni(OEiBC)] or a greater than 20-fold excess of bromine. Each complex underwent a one-electron oxidation. The hydroporphyrin complexes also suffered small amounts (about 0–10%) of oxidative dehydrogenation, which afforded the next most unsaturated macrocycle in the series. Dehydrogenation was more prevelant for Ni(OEiBC) than for Ni(OEC). Except for the presence of small amounts of the dehydrogenation products, the UV–vis spectra of chemically oxidized complexes were identical with those obtained by spectroelectrochemical means. Attempts to prepare $Ni(OEC)^{2+}$ or $Ni(OEiBC)^{2+}$ by chemical oxidation with the tris(*p*-bromophenyl)amminium salt or with larger excess of bromine were frustrated by the instability of the complexes under these conditions.

The EPR spectra of the one-electron-oxidized complexes established that they were nickel(II) cation radicals. The site of oxidation was neither affected by the identity of the chemical oxidant nor affected by cooling to liquid-nitrogen temperatures. Solutions of these complexes did not change color on cooling. The EPR spectra of $Ni(OEP)^{\bullet+}$ in methylene chloride, both at room temperature and as a glass at 100 K, consisted of a single line at $g = 2.003$ that was devoid of resolvable hyperfine structure and had a line width of 8 G. The spectra agreed with that obtained by ferric perchlorate oxidation of Ni(OEP) in chloroform/methanol solution.[13,15] A single line at $g = 2.006$ with a line width of 9.0 G was observed for $Ni(OEC)^{\bullet+}$, in agreement with the spectrum reported previously for this radical.[15] The EPR spectrum of partially oxidized solutions of Ni(OEiBC) consisted of a single line at $g = 2.005$ and had a 14.0 G line width.

Discussion

Our data unequivocally establish that the first oxidations of Ni(OEP), Ni(OEC), and Ni(OEiBC) yield nickel(II) cation radical complexes. Unlike $Ni(TPP)^{\bullet+}$, internal electron transfer to form nickel(III) complexes did not occur when these complexes were cooled to liquid-nitrogen temperatures under our experimental conditions. Although EPR spectra of $Ni(MOEC)^{+}$ and $Ni(DMOEiBC)^{+}$ were not obtained, the near equivalence of potentials of the first oxidations of nickel complexes in the methylated octaethyl- and octaethylhydroporphyrin series suggest that $Ni(MOEC)^{+}$ and $Ni(DMOEiBC)^{+}$ are also nickel(II) cation radicals.

Identification of the products of the second oxidations is somewhat problematical. Magnetic properties provide the best criteria for distinguishing nickel(II) dication complexes from nickel(III) cation radical complexes. Dication complexes are dimagnetic and therefore EPR silent. The two spins of the nickel(III) cation radical complex can interact in several distinct ways.[14] The unpaired electron of nickel(III) resides in the d_{z^2} orbital. Because this orbital and the porphyrin π orbital that contains the second unpaired electron are orthogonal, ferromagnetic coupling of the spins is expected. The ground state will be a triplet with an expected spin-only magnetic moment of 2.83 μ_B. Deviations of the nickel from the plane of the four nitrogens can relax the orthogonality of the orbitals, however, and lead to antiferromagnetic coupling of the spins. An EPR spectrum of the triplet may or may not be observable, depending upon the size of the zero-field splitting. Unfortunately, the instability of $Ni(OEC)^{2+}$ and $Ni(OEiBC)^{2+}$ produced by chemical oxidation precludes EPR spectroscopic and magnetic characterizations. Thus, identification must be based upon the absorption spectra and electrochemical properties of doubly oxidized complexes. It has been pointed out that absorption spectra are not always reliable criteria when the central metal is not diamagnetic.[14]

The solvent dependence of the potentials of the second oxidation of nickel hydroporphyrin complexes, which was discussed above, provides circumstantial evidence for formation of nickel(III) cation radical complexes in at least the more strongly coordinating solvents. The UV–vis spectrum of $Ni(OEiBC)^{2+}$ in CH_3CN, Figure 5, is consistent with this suggestion. The spectrum is quite unlike that of authentic dications including $Zn(OEiBC)^{2+}$. On the other hand, the spectrum generally resembles those of cation radicals including $Ni(OEiBC)^{\bullet+}$. Small alterations in spectra upon oxidation are more typical of metal-based rather than macrocycle-based oxidation (particularly if the metal remains diamagnetic in the second case). Thus, our data suggest that $Ni^{III}(OEiBC)^{\bullet 2+}$ is the correct description for the complex. On the other hand, the spectra of $Ni(OEP)^{2+}$ in CH_2Cl_2 and of $Ni(OEC)^{2+}$ in CH_3CN establish that these complexes are nickel(II) dications. Our data does not rule out the possibility that $Ni^{III}(OEC)^{\bullet 2+}$ is produced in DMF, however.

Data for nickel tetraaza macrocyclic complexes demonstrates that nickel(III) is more readily accessible for macrocycles with smaller hole sizes or larger ligand field strengths.[33,34] The accessibility of nickel(III) when coordinated to an $OEiBC^{\bullet+}$ macrocycle (in weakly coordinating solvents like CH_3CN) but not when corrdinated to $OEP^{\bullet+}$ or $OEC^{\bullet+}$ suggests that the ligand field/hole size of these oxidized macrocycles are different. We have demonstrated recently that the ligand field/hole sizes of the neutral macrocycles are indeed different.[17] The difference arises in part from the smaller change in conformational energy required to distort hydroporphyrin macrocycles from planarity compared with porphyrins. Such distortions can decrease (ruffling) or increase (doming) the metal–nitrogen bond distances. For low-spin nickel(II) complexes, the steepness of the S_4 ruffle increases with increasing saturation of the macrocycle.[6,7c] Although extrapolation from the neutral macrocycles to the oxidized macrocycles is hazardous, apparently $OEiBC^{\bullet+}$ can ruffle more deeply to contract its core to the greatest extent and best stabilize nickel(III).

Finally, we return to the question of the stabilization of oxidized *cis*-OEC species by coordination to nickel. We have shown that *trans*-$Ni(OEC)^{2+}$ is best formulated as a nickel(II) dication in acetonitrile solution, the same solvent in which the stabilization of the cis complexes was observed.[1] It would seem likely that *cis*-$Ni(OEC)^{2+}$ is also a nickel(II) dication complex. *cis*- and *trans*-Ni(OEC) are oxidized at nearly identical potentials. To postulate that *cis*-$Ni(OEC)^{2+}$ is a nickel(III) cation radical would require that *cis*-$(OEC)^{\bullet+}$ be able to ruffle more deeply and stabilize nickel(III) better than *trans*-$(OEC)^{\bullet+}$. Precisely the opposite appears to be true for the neutral OEC compounds. The barrier to inversion of the sense of ruffling is smaller for *cis*-Ni(OEC) than for *trans*-Ni(OEC), suggesting that the extent of ruffling is also smaller.[1] Nonetheless, *cis*-Ni(OEC) *is* ruffled in solution.[1] Therefore, our conclusion that *cis*-$Ni(OEC)^{2+}$ is a nickel(II) dication strongly suggests that the enhanced stability of the oxidized *cis*-Ni(OEC) complexes arises from the ruffled conformation of the macrocycle. Thus, the chemical reactivity of metallotetrapyrrole complexes can be significantly affected by the conformation of the macrocycle.

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Acknowledgment. We thank Dr. William H. Orme-Johnson and Neil Bastian for assistance in obtaining EPR spectra and the Camille and Henry Dreyfus Foundation (Young Faculty Grant to A.M.S.), the Research Corp., and the National Institutes of Health (Grant GM 33882) for support of this research.

Registry No. H_2(OEP), 2683-82-1; $H_2(OEP)^+$, 43078-00-8; $H_2(OEP)^{2+}$, 113773-40-3; H_2(OEC), 991-74-2; $H_2(OEC)^+$, 113773-46-9; $H_2(OEC)^{2+}$, 113773-41-4; H_2(OEiBC), 72260-12-9; $H_2(OEiBC)^+$, 73069-22-4; $H_2(OEiBC)^{2+}$, 73068-83-4; H_2(MOEC), 74071-46-8; $H_2(MOEC)^+$, 113686-71-8; $H_2(MOEC)^{2+}$, 113773-42-5; H_2(DMOEiBC), 113686-70-7; $H_2(DMOEiBC)^+$, 113686-72-9; $H_2(DMOEiBC)^{2+}$, 113773-43-6; Ni(OEP), 24803-99-4; $Ni(OEP)^+$, 74876-13-4; $Ni(OEP)^{2+}$, 24803-99-4; Ni(OEC), 28375-46-4; $Ni(OEC)^+$, 113773-44-7; $Ni(OEC)^{2+}$, 113773-45-8; Ni(OEiBC), 39001-94-0; $Ni(OEiBC)^+$, 113686-73-0; $Ni(OEiBC)^{2+}$, 113686-74-1; Ni(MOEC), 113686-75-2; $Ni(MOEC)^+$, 113686-76-3; $Ni(MOEC)^{2+}$, 113686-77-4; Ni(DMOEiBC), 113686-80-9; $Ni(DMOEiBC)^+$, 113686-78-5; $Ni(DMOEiBC)^{2+}$, 113686-79-6; $[(p\text{-}BrC_6H_4)_3N][SbCl_6]$, 24964-91-8; $[(p\text{-}CH_3C_6H_4)_3N][SbCl_6]$, 65644-87-3; Br_2, 7726-95-6.

Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer. 91. Reactions of Carboxylato-Bound Chromium(V) with Arenediols[1]

S. K. Ghosh, Rathindra N. Bose,[2] and E. S. Gould*

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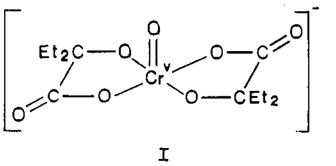
The chromium(V) chelate bis(2-ethyl-2-hydroxybutanoato)oxochromate(V) (I) oxidizes the arenediols hydroquinone and 2,3-dihydroxybenzoic acid in solutions buffered with the ligand acid, 2-ethyl-2-hydroxybutanoic acid, and its anion. The observed 1:1 stoichiometry of these reactions corresponds to the formation of the related quinone and Cr(III). The Cr(III) product from the reaction of excess hydroquinone is a bis chelate derived from the ligand anion, having, in addition, a ligand derived from the diol. With 2,3-dihydroxybenzoic acid, the diol appears to have coordinated to Cr(III) as a bidentate ligand. Both reactions are catalyzed by Cr(IV) and pass through semiquinone radicals, $ArO_2H^•$, for which Cr(IV) and Cr(V) compete. Suggested reaction sequences for the two reductants feature bimolecular steps involving Cr(V) + $Ar(OH)_2$, Cr(V) + $ArO_2H^•$, and Cr(IV) + $ArO_2H^•$ (reactions 3, 4, and 6 in the text) but differ in the reaction of Cr(IV) with $Ar(OH)_2$, which is bimolecular with hydroquinone but exhibits kinetic saturation with 2,3-dihydroxybenzoic acid, indicating the formation of a strongly associated complex of the latter with Cr(IV). The suggested reaction sequences, in conjunction with rate constants for the individual steps derived from least-squares refinements of the data, reproduce the experimental kinetic curves. Dependencies of the component specific rates on the concentration of the ligand anion, [Lig^-], indicate that partition of Cr(V) and Cr(IV) between ligation levels affects the reactions with hydroquinone but not those with dihydroxybenzoic acid. Acid catalysis of the Cr(IV)–$Ar(OH)_2$ step (k_5) for the latter diol points to partial protonation of the Cr(IV)–diol complex (pK = 3.5). Comparisons of calculated electron-transfer rates with those for known outer-sphere reactions indicate that at least three of the four steps involving each diol proceed through bridged activated complexes. In contrast to earlier systems utilizing the proposed mechanism, the prominence of autocatalysis in the oxidation of hydroquinone is limited by the poor selectivity (Cr^{IV} vs Cr^V) of the semiquinone radical rather than by the selectivity of the diol itself. Autocatalysis is not observed in the oxidation of 2,6-dihydroxynaphthalene.

In our investigations of the redox chemistry of carboxylato complexes of chromium(V),[3] we have encountered considerable diversity in kinetic behavior. The 2e reductants Sn^{II}, H_2O_2, and N_2H_4 generate uncomplicated exponential decay curves.[4] This apparent simplicity extends also to reductions by Ti^{III} and $IrCl_6^{3-}$ despite the intervention of Cr(IV),[4a,5] for these donors react much more rapidly with Cr(IV) than with the less strongly oxidizing state[6] Cr(V). With VO^{2+} and Fe^{2+},[7] specific rates for the two successive steps are more nearly the same, and the buildup and loss of a Cr(IV) transient are clearly reflected in biphasic traces.

With reductants having both 1e and 2e capabilities, at least four different transfers may occur. Suitable interrelationships between rates for such components may lead to autocatalysis,[3,6a,8] and in some instances, the Cr(IV) intermediate is seen to grow slowly but decay suddenly, leading to a kinetic profile typifying a clock reaction.[6a,8a,c] Although autocatalytic reductions were initially described for the inorganic anions bisulfite,[6a] hypophosphite,[8b] and iodide,[8a] analogous behavior has been noted also for the organic reductants ascorbic acid,[8c] thiolactic acid,[9] and cysteine.[9] Each of these may undergo 1e oxidation to an organic radical which, in turn, rapidly reacts with both Cr(V) and Cr(IV).

The present report deals with reactions of the $Cr^V(=O)$ bis chelate of 2-ethyl-2-hydroxybutyric acid (I) with several dihydroxybenzene derivatives having structures allowing their conversion to quinones. With diols it was anticipated that intervention of 1e oxidation products, semiquinones, might be reflected in mechanistic variation. Although a number of such systems were characterized by unusually complex kinetic patterns



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[2] Present address: Department of Chemistry, Pittsburg State University, Pittsburg, KS 66762.

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