has been attributed to a smaller degree of solvent-aided dissociation of the halide group in the transition state. In H_2O at 65° and at pH 2, the value of k_{obsd} is 27% higher than at pH 0 because of the acid dissociation of the bromoaquo species. In D_2O, however, the increase in k_{obsd} in going from pH 0 to pH 2 is is only 17%. This observation is consistent with an acid–base equilibrium in which the acidic species aquates slower, since it has been established previously that weak acids are less dissociated in D_2O than in H_2O.[15]

The opposite effect has been observed in the acid-catalyzed aquation of *trans*-$Co(en)_2F_2^+$ since, in this case, the protonated species reacts faster.[16]

A final point of interest in this study is a comparison of the primary and secondary aquation constants for $Co(tren)Br_2^+$ with those of similar complexes. As stated previously, the value of k_1 for the aquation of $Co(tren)Br_2^+$ is 27 times larger than that for *cis*-$Co(en)_2Br_2^+$ at 25° and is 10 times larger than that of *cis*-$Cr(en)_2Br_2^+$.[4] This increased aquation rate in the tren complex has been attributed to a distortion of the complex by the tren ligand, which causes both a strain in the complex and an increased exposure of the bromide ligands to the solvent.[6a] The effect of this distortion would then be to labilize the bromide groups in either an SN1 or an SN2 mechanism. A similar comparison of the second aquation steps of these complexes, however, shows that the value of k_2 for the aquation of the tren complex at 25° is almost $^1/_{58}$th as fast as that for *cis*-$Cr(en)_2H_2OBr^{2+}$.[4] Furthermore, although no data are available for the aquation of *cis*-$Co(en)_2H_2OBr^{2+}$, a comparison of the value of k_2 for the aquation of *cis*-$Co(en)_2H_2OCl^{2+}$[5] with that of $Co(tren)H_2OBr^{2+}$ at 25° shows that the tren complex aquates only twice as fast, while $Co(tren)Br_2^+$ aquates over 100 times faster than *cis*-$Co(en)_2Cl_2^+$ at the same temperature.

The marked decrease in labilization of the second bromide ion relative to that of the first can only be explained by a reduction in the distortion of the complex after the loss of the first bromide ion. This is not unreasonable, since the replacement of a bulky *cis* bromide group by water, combined with the increased positive charge of the complex, would allow the second bromide group to be pulled in closer to the cobalt and hence decrease its vulnerability to solvent attack by an SN2 mechanism. The increase in $\Delta S^{\ddagger}$ of the second aquation step relative to that of the first is consistent with a decrease in SN2 character for the aquation of the bromoaquo species, although the mechanism is undoubtedly of mixed SN1 and SN2 character.

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Electron Paramagnetic Resonance Identification of a Nickel(III) Compound Produced by Electrochemical Oxidation of Nickel(II) Tetraphenylporphyrin

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In complexes with certain large organic chelating ligands it is difficult to assign the true valency state of the metal ion.[2] Therefore, there has been a controversy over the identification of Ni(III) and NI(IV) species in solution.[3–7] The critics[6,8] of the Ni(III) assignment base their arguments on the expected difference between a free-radical type and a $3d^7$ type epr signal. Magnetic susceptibility is not sensitive enough to distinguish between the two. More recently additional claims of Ni(III) species in solution were made;[9–11] however, attempts to observe the epr signal either failed[9] or were not reported.[10,11] During our studies of the physical properties in solution of the iron through zinc tetraphenylporphyrins[12] we have found evidence for the existence of a nickel(III) tetraphenylporphyrin cation.

Experimental Section

Nickel tetraphenylporphyrin, $Ni^{II}TPP$, was synthesized according to ref 13. A 10^{-3} *M* solution of $Ni^{II}TPP$ in 0.1 *M* $(C_4H_9)_4NClO_4$–benzonitrile was prepared. The solvent was purified by passing it over a column of alumina adsorbent just prior to its use, to ensure anhydrous conditions.

The electrochemical oxidation was studied by cyclic voltammetry and controlled-potential coulometry, using a Wenking 66TS10 potentiostat in conjunction with a Hewlett-Packard 3300A function generator, using a saturated aqueous calomel electrode as reference. Oxidation products obtained by controlled-potential electrolysis were transferred into a flat cell or sealed quartz ampoule and were studied on an X-band Varian Associates 4502 epr spectrometer, equipped with a Hewlett-Packard X530A frequency meter and using peroxylaminedisulfonate ion as a standard. Optical spectra were measured on a Coleman Hitachi 124 double-beam spectrometer.

Results

Figure 1 displays a cyclic voltammogram taken at

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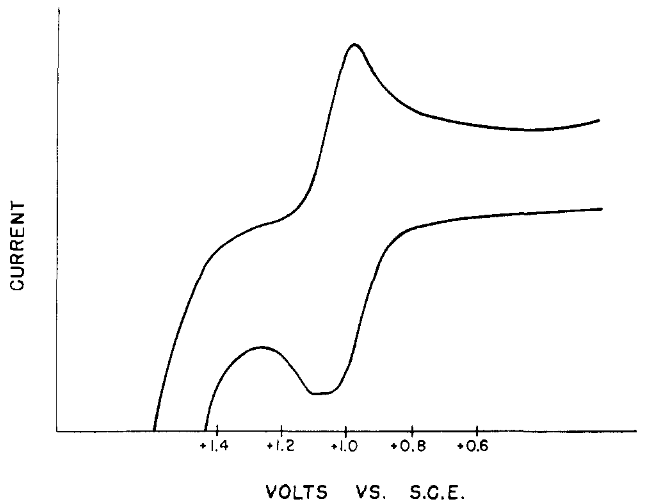

Figure 1.—Cyclic voltammogram of the $Ni^{II}TPP$ system; 10^{-3} *M* solution in 0.1 *M* $(C_4H_9)_4NClO_4$–benzonitrile, scan rate 0.125 V/sec.

the original $Ni^{II}TPP$ optical spectrum was observed. The epr signal of the oxidation product obtained by electrolysis could not be observed at room temperature, as was the case for the neutral $Co^{II}TPP$ complex.[12,15] The signal at liquid nitrogen temperature displayed axial symmetry and was the same either after oxidation at 0.95 or 1.2 V or any value in between. After leaving the oxidized solution at room temperature for a while a new symmetric very weak signal developed which could

TABLE I

EPR DATA

Species	Temp, °K	g_{av}[a]	$g_{\parallel}$	$g_{\perp}$
$Ni^{III}TPP^+$	295		Not observed	
	77	2.235	2.116	2.295
$Ni^{II}TPP\cdot^+$	295	2.027		
	77	2.026	2.031	2.024
$H_2TPP\cdot^+$	295	2.011		
	77	2.011	2.009	2.013

[a] Experimental error ±0.001.

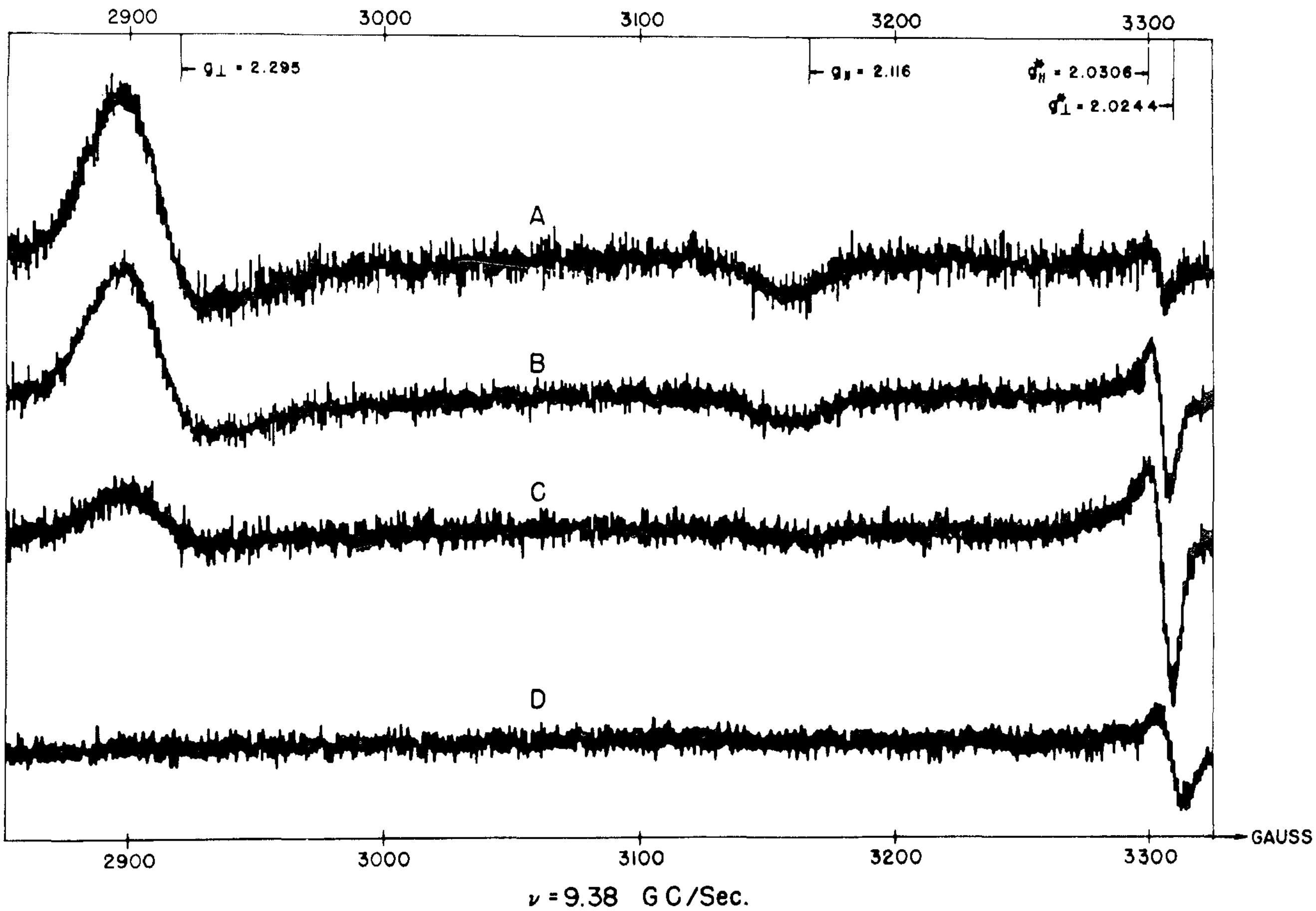

Figure 2.—Epr spectra of $Ni^{III}TPP^+$ and $Ni^{II}TPP\cdot^+$ (starred *g* values) at 77°K (A) 10 min, (B) 30 min, (C) 100 min, and (D) 280 min after the end of the electrochemical oxidation.

room temperature. It is consistent with the theoretical predicted curve of Polcyn and Shain[14] for the case of two overlapping successive one-electron-transfer steps, in which the first process is a reversible one and the second an irreversible one. The overall cycle is reversible, in the sense that after a complete controlled-potential cycle (oxidation at 1.3 V, reduction at 0.7 V)

be observed at room temperature. At liquid nitrogen temperature this signal was slightly asymmetric. The intensity of the original signal constantly decreased. Both spectra satisfy a spin Hamiltonian of effective spin $^1/_2$. The *g* factors of the asymmetric signals were calculated by comparing the experimental curves with simulated ones.[16] The *g* factor for the symmetric

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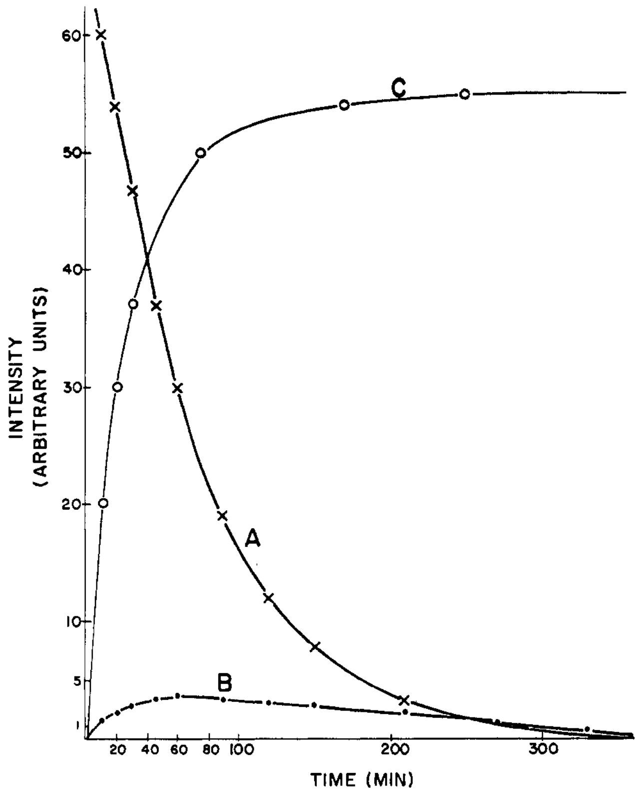

Figure 3.—Concentration change with time of $Ni^{III}TPP^+$ (A), $Ni^{II}TPP^+$ (B), and $Ni^{II}TPP$ (C); A and B measured by epr; C, by optical spectroscopy.

signal was measured directly from the experimental spectrum. Table I summarizes the epr data of the two Ni compounds and that of the nonmetallic oxidation product, $H_2TPP\cdot^+$.[12] Figure 2 gives the variation of the two signals with time. The intensity variation with time of the two epr signals and the optical intensity recovery (~96%) of the Soret band (418 mμ) peak height of the $Ni^{II}TPP$ complex indicate a consecutive reaction mechanism (Figure 3), with a rate constants ratio of about 10.

Discussion

The two epr signals are sufficiently distinct to assign the first one to a square-planar d^7 configuration,[17] compatible with $Ni^{III}TPP^+$ cation, and the second one to a free-radical ion, $Ni^{II}TPP\cdot^+$, in which the unpaired electron is associated with the ligand π system. The oxidized nonmetallic ligand has different g values. These epr results combined with trends we found for oxidation behavior in the series iron–zinc TPP[12] suggest that the first oxidation produces the $Ni^{III}TPP^+$ cation. The second oxidation product is apparently $Ni^{III}TPP^{2+}$ rather than $Ni^{IV}TPP^{2+}$.[12] This species, which we see by cyclic voltammetry, is unstable and rapidly returns to the $Ni^{III}TPP^+$ cation *via* an electron capture. This oxidation mechanism is consistent both with the epr result that only one signal is produced after oxidation at various potentials and with the observation that the area under the reduction peak in the cyclic voltammogram is more than half of the area of the oxidation peak (Figure 1). This type of cyclic voltammogram precludes the possibility of having one-step two-electron transfer. The optical spectrum of the two-electron oxidized species could not be obtained without interference from the decomposition products, which in turn could not be observed at all under our experimental conditions (see Figure 1 of ref 12). The $Ni^{III}TPP^+$ cation, which is the monooxidation product, slowly decomposes to the original $Ni^{II}TPP$ complex by way of the cation radical $Ni^{II}TPP\cdot^+$ (Figure 3). The decomposition mechanism of $Ni^{III}TPP^+$ to the free-radical cation $Ni^{II}TPP\cdot^+$ is uncertain. The overall reaction is a ligand-to-metal atom electron transfer; however, at the present time we do not have enough data to determine the detailed mechanism.

However, regardless of the exact decomposition mechanism and despite the strong covalency in metalloporphyrins by observing the two different epr signals, we could distinguish between the metal and the ligand oxidation products of the $Ni^{II}TPP$ complex. Therefore, we believe that in this case we have actually identified a planar Ni(III) complex with a $3d^7$ configuration,[17] as opposed to assigning a formal oxidation state of 3 with an undetermined configuration.

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An Oxygen-18 Study of the Reaction between Iridium- and Platinum-Oxygen Complexes and Sulfur Dioxide to Form Coordinated Sulfate

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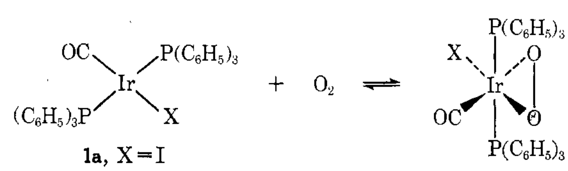
In 1963, the remarkable iridium(I) complex **1** was found to form reversibly a 1:1 complex with O_2.[3] In the intervening years, diamagnetic mononuclear oxy-



1a, X = I
b, X = Cl
2

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