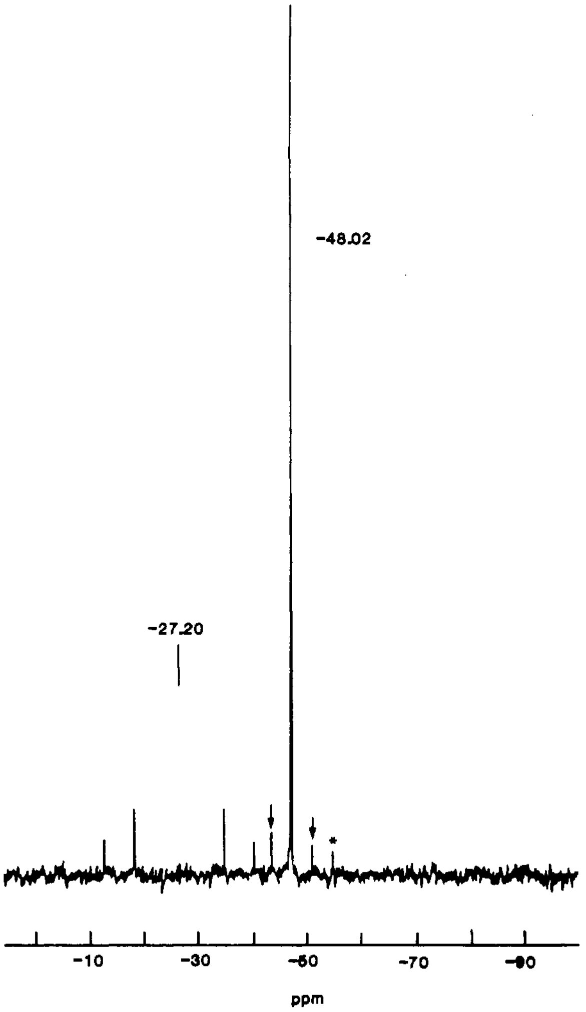
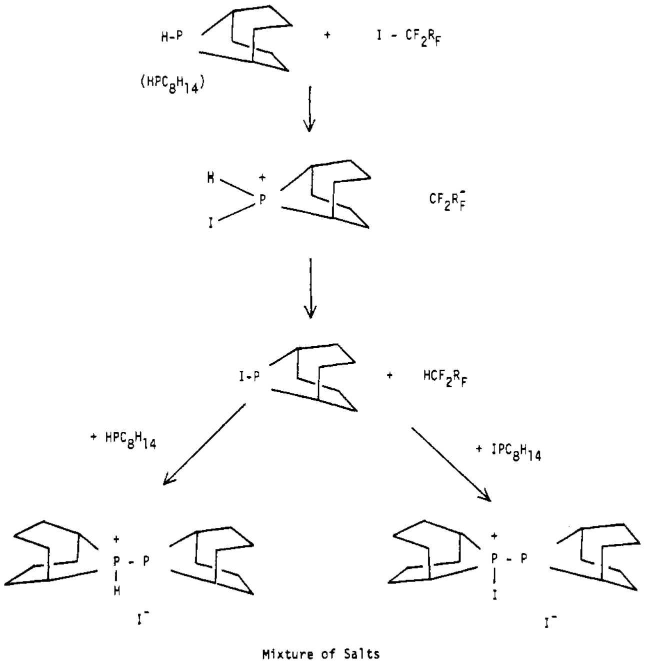


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of $C_8H_{14}PPC_8H_{14}$ in benzene-d_6. The peaks marked with arrows (↓) are 120-Hz sidebands, and the peak marked with an asterisk is due to HPC_8H_{14}.

Scheme I



with *n*-butyllithium in diethyl ether at 0 °C gave the phosphide $LiPC_8H_{14}$ in >80% yield, which reacted with 1-bromohexane to give $C_6H_{13}PC_8H_{14}$. A similar reaction between the phosphide and C_3F_7I gave small amounts of both $C_8H_{14}PPC_8H_{14}$ and a species presumed to be $C_3F_7PC_8H_{14}$.[6]

In another potential synthetic route to $C_8H_{14}PPC_8H_{14}$, HPC_8H_{14} was reacted with triphenylmethyl cation at reflux in THF for 1 week. The product was a salt that was inferred to contain the cation $PC_8H_{14}^+$[19] by reaction with hexylmagnesium bromide giving $C_6H_{13}PC_8H_{14}$. Reaction of $LiPC_8H_{14}$ (see above) with $PC_8H_{14}^+BPh_4^-$[19] led to the formation of an unidentified product with only small amounts of the expected diphosphine.

Since bulky phosphines are known to increase the linear/branched ratios (*L*/*B* ratio) of products in the cobalt-catalyzed hydroformylation reaction,[20] we compared the oxo product obtained with the diphosphine-modified catalyst to that obtained with a related tertiary phosphine ($C_6H_{13}PC_8H_{14}$) under identical conditions (3500 psig 1:1 CO/H_2, 180 °C). Periodic product sampling during the reaction showed that the diphosphine gave $L/B = 9$ up to 50% olefin conversion, the same as was observed with the monophosphine $C_6H_{13}PC_8H_{14}$. However, above 50% conversion the *L*/*B* ratio dropped drastically so that $L/B = 1.17$ in the final product was similar to that observed with unmodified cobalt catalysts. This suggests that some thermal decomposition of the diphosphine had occurred. This decrease of the *L*/*B* ratio was not observed with the monophosphine $C_6H_{13}PC_8H_{14}$. Under these conditions, an unmodified cobalt catalyst gives a mixture of aldehyde and alcohol with low linearity ($L/B = 1$), while addition of a phosphine ligand modifier increases production of alcohol product and gives higher *L*/*B* ratios.

The loss of high linear/branched ratio must be due to some ligand decomposition process. Reaction of a tetramethyl diphosphine with an iron complex followed by proton abstraction[21] has been shown to give a coordinated R_2PH ligand. In a recent report,[22] phosphido ligands in phosphido-bridged cobalt carbonyl oxo catalysts apparently reacted with metal hydride or H_2 to give coordinated R_2PH ligands, which reacted further with olefin to give a tertiary phosphine. In the present case, if cleavage of the diphosphine giving phosphido groups occurred, further reaction to give tertiary phosphine ligands did not occur, as the high *L*/*B* product ratios typical of tertiary phosphine oxo modifiers were not maintained through the entire reaction. It is probable that decomposition of the diphosphine involves some other mechanism, such as reaction with the acidic hydrogen of the aldehyde product.

Acknowledgment. We would like to acknowledge the able assistance of Cliff Turpin in the synthetic work and to thank Gulf Research & Development Co. for support and permission to publish this work. Special thanks are due Dr. J. J. Harrison for valuable discussions of mechanism.

Registry No. C_3F_7I, 754-34-7; $Co_2(CO)_8$, 15226-74-1; PH_3, 7803-51-2; 9-phosphabicyclo[4.2.1]nonane, 13396-80-0; 9-phosphabicyclo[3.3.1]nonane, 13887-02-0; 2,2′-azobis(2-methylpropionitrile), 78-67-1; hexyl bromide, 111-25-1; dodec-1-ene, 112-41-4.

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Spontaneous Oxidation of Metallotetraphenylporphyrins on Porous Vycor Glass

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Received February 11, 1985

For tetraphenylporphyrin (TPP) and metallotetraphenylporphyrins (MTPP) the first oxidation of the TPP ring occurs at a half-potential of about 1 V (vs. SCE) and gives rise to a well-characterized porphyrin π cation radical.[1] A second oxidation

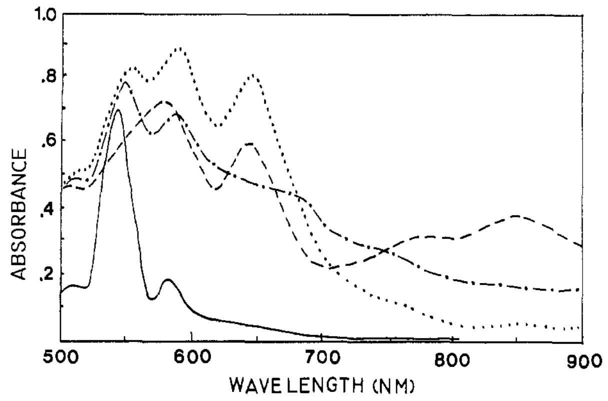

Figure 1. Absorption spectra of ZnTPP in methylene chloride solution (—) and at various times after adsorption onto porous Vycor glass (PVG): (-•-) 30 min; (•••) 48 h; (--) 7 days.

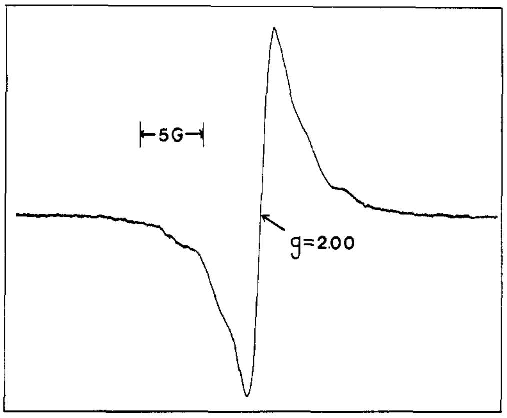

Figure 2. Room-temperature electron paramagnetic resonance spectrum, at 9.7 GHz, of ZnTPP adsorbed onto powdered PVG and then evacuated to remove solvent. Spectrum obtained with 4 mW microwave power, with 100-kHz modulation (0.4 Gpp) and a gain of 2×10^5.

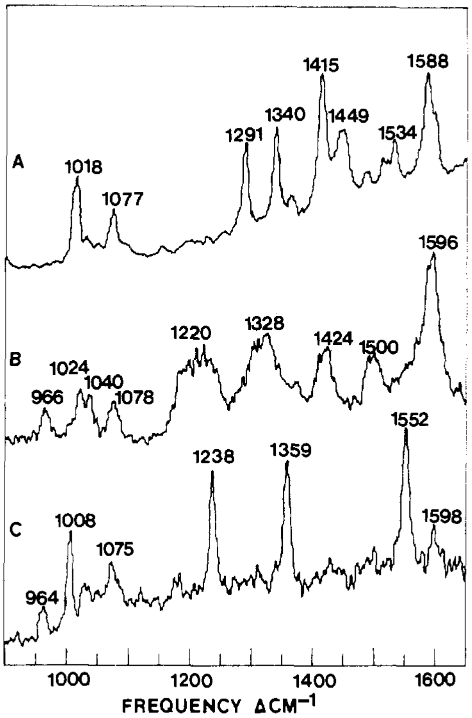

Figure 3. Resonance-enhanced (457.9 nm) Raman spectra: (A) isoporphyrin from ceric oxidation of ethanolic ZnTPP; (B) PVG adsorbate of ZnTPP (3 days); (C) ZnTPP mixed with KBr. All spectra were recorded with approximately 5-cm^{-1} spectral slit widths.

can occur, typically at a few tenths of a volt higher potential. This generates a dication, which is subject to nucleophilic attack and conversion to an isoporphyrin form, reduced at the methine carbon.[2] These oxidations are usually carried out by chemical (e.g. bromine or ceric ion) or electrochemical means.

We report here the spontaneous oxidation of the tetraphenylporphyrin ring for ZnTPP and TPP upon adsorption from methylene chloride solution, in air, onto the surface of Corning Code No. 7930 porous Vycor glass (PVG). The oxidation products have been characterized by visible absorption, resonance Raman, and electron paramagnetic resonance spectra.

Results and Discussion

Adsorption of ZnTPP (or TPP) from methylene chloride solution onto the surface of PVG, followed by removal of solvent in vacuo, results in conversion of the red-purple solution to a green adsorbate. The visible absorption spectrum of ZnTPP on the glass, immediately upon solvent removal (Figure 1), indicates the loss of ZnTPP (decrease of the 555-nm band) and formation of product(s) absorbing to the red (600–900 nm). Significant initial spectral changes are observed within the time required to adsorb from solution and pump off solvent (~30 min), but further changes continue to be observed for several days (see Figure 1). A notable feature of these spectra, which are quite prominent after several days, are peaks at 850 and 770 nm. These increase with time over several days. These absorption peaks are indicative[2] of the presence of isoporphyrin, which has been reported[2] to form via nucleophilic attack at the methine carbon on the oxidized dication of ZnTPP and other MTPP's. No other well-characterized porphyrin derivative shows characteristic absorption features in this spectral region. The reported absorption maxima for the isoporphyrin produced by addition of methanol to a solution of the dication of ZnTPP are at 440, 780, and 860 nm. Other absorption bands in the spectrum of the PVG adsorbate are attributable to the as yet uncharacterized oxidation products and/or demetalated, protonated TPP.

Examination of the electron paramagnetic resonance (EPR) spectrum of ZnTPP (or TPP) adsorbed onto powdered PVG in air and then evacuated and maintained in vacuo revealed a strong signal centered at $g = 2.00$, with a line width (Figure 2) consistent with that reported for the π cation radical of ZnTPP in solution.[3] If powdered PVG is treated identically with solvent only, no EPR signal is detectable in this region. Although splittings observed in reported EPR spectra for solution species are much better resolved, close inspection of Figure 2 reveals a barely resolved splitting pattern, again, consistent with the nine-line pattern expected due to four equivalent nitrogens of the TPP ring. Our inability to better resolve these splittings for the adsorbed species is attributable to the necessarily heterogeneous nature of the radical species population induced by interaction with the PVG surface, as well as the powderlike spectrum expected for a sample that approximates a frozen solution.

Upon introduction of air to the EPR tube, the radical signal disappears completely, but can be regenerated by evacuating for several minutes. This cycle can be repeated several times with some loss of signal intensity. The complete, though largely reversible, loss of EPR signal intensity in the presence of air suggests some specific chemical quenching of the radical species. Because of the reversibility upon evacuation, some type of oxygen adduct of the radical species may be involved. The requirement of oxygen for cation radical formation was demonstrated by preparing a sample for an EPR experiment in the absence of oxygen. No EPR signal was detectable, and no characteristic color change was observed when ZnTPP was adsorbed in the absence of oxygen.

All samples were routinely prepared, handled, and stored without precautions to exclude light. When otherwise identical duplicate samples were separately incubated in the dark or nor-

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Inorg. Chem. **1985**, *24*, 4441–4444

mally exposed to laboratory light, no significant differences were noted in the absorption spectra (460–900 nm) as a function of time.

The resonance Raman spectrum using 457.9-nm excitation (900–1650 cm^{-1}), in air, of the ZnTPP adsorbed onto PVG (Figure 3B) is quite distinct from the spectrum of solid ZnTPP (Figure 3C) or the previously reported[4] spectra of the cation radical in solution. In the spectral region above 900 cm^{-1}, a band at 1596 cm^{-1} is most prominent in the PVG-adsorbed sample, whereas solid ZnTPP shows several equally prominent bands at 1552, 1359, and 1238 cm^{-1}. The previously reported resonance Raman spectrum of the ZnTPP cation radical is not unlike that of ZnTPP, showing only small frequency shifts from the ZnTPP spectrum. The resonance-enhanced Raman spectrum of the isoporphyrin generated by ceric oxidation of an ethanolic solution of ZnTPP (Figure 3A) shows a strong band at 1588 cm^{-1} in the high-frequency spectral region. There is no evidence of the strong 1552-cm^{-1} ZnTPP band in the PVG adsorbate spectrum. The same is true of the 1359-cm^{-1} band. The broad features in the PVG adsorbate spectrum (Figure 3B) at 1424 and 1328 cm^{-1} may correspond to isoporphyrin bands at 1415 and 1340 cm^{-1}, respectively, in Figure 3A. The broadness of these Raman features for the PVG adsorbate spectrum is attributable to the heterogeneity of the reaction products being sampled (see discussion of the absorption spectrum above). An additional contribution to heterogeneity is likely due to the fact that various surface silanol groups and/or surface-bonded water molecules are the nucleophiles active in forming isoporphyrin. The Raman band at 1596 cm^{-1} is reasonably assigned as the analogue to the 1552-cm^{-1} ZnTPP band, upshifted by 44 cm^{-1} due to the reduction in the π-conjugation path for the methine-reduced isoporphyrin species. This is also reflected in the large changes seen in the visible spectra. The 457.9-nm resonance excitation favors the selection of Raman scattering from the isoporphyrin species on the glass because of the associated 440-nm Soret band. Resonance Raman spectroscopy using excitation to the red of 457.9 nm is prohibited by strong luminescence, which swamps the Raman signals. The possible photodegradation of adsorbed metalloporphyrin was minimized by defocusing the laser excitation source. Rescanning of key spectral regions to assure constant scattering levels was used to monitor for photodegradation.

Although not anticipated, the oxidation of an adsorbate by PVG is not unique. A previous report[5] details the oxidation of 1,1-diphenylethylene (DPE) upon adsorption onto PVG. This oxidation also produced a cation radical species, which was stabilized and detected spectroscopically. The DPE oxidation was attributed to Lewis acid sites on the PVG surface. The oxidation of ZnTPP and TPP reported here indicates that such sites may act as oxidizers for a wider variety of molecules.

In contrast to our findings, Raman studies[6] of NiTPP adsorbed onto more conventional supports such as silica and alumina fail to show any adsorption-induced changes. Furthermore, heating NiTPP adsorbed on silica at 300 °C in nitrogen produced no spectral changes before the onset of decomposition. Similar experiments on alumina produced only relative intensity changes in the Raman bands before decomposition set in.

In summary, the resonance Raman and absorption spectra establish the presence of isoporphyrin species on the PVG surface after adsorption of ZnTPP. Previous studies have shown that these arise via nucleophilic attack on the dication produced by oxidation of the ZnTPP. On the PVG surface, adsorbed water and/or silanol groups would be the likely nucleophiles. The formation of oxidized ZnTPP is evidenced by the EPR spectra of the π cation radical form for both ZnTPP and TPP. The dication is not directly observed in any of our experiments, but its presence is inferred from the isoporphyrin substitution product. Further, the nature of the oxygen dependence of the EPR signal indicates that some type of oxygen adduct of the radical may be involved in the route leading to isoporphyrin formation. No significant reaction occurs if ZnTPP is adsorbed in the absence of oxygen.

Experiments with several other metallotetraphenylporphyrins, including Fe^{III}(TPP)Cl, CuTPP and Ru(CO)TPP indicate that these oxidations are a general phenomenon associated with adsorption onto the PVG surface. Further characterization of these reactions is continuing in our laboratory.

Experimental Section

ZnTPP and TPP were purchased from Man-Win Chemical Co. and subjected to chromatography on alumina before use. All solvents were spectroquality grade. Samples were adsorbed onto pretreated PVG as previously described.[7,8] For Raman and optical absorption measurements, pieces of PVG about 25 mm × 25 mm × 4 mm were used. For EPR experiments, the PVG was crushed into pieces small enough to fit a 3-mm-i.d. quartz EPR tube, before adsorption experiments.

Absorption spectra were recorded on a Cary 14 or a Perkin-Elmer Lambda 3 UV–visible spectrophotometer. Electron Paramagnetic Resonance spectra were recorded on an IBM Instruments ER200E-SCR EPR machine (9-in. magnet). Resonance Raman spectra were recorded by using a previously described system.[9]

Acknowledgment. Support for this research by the City University of New York research awards program and the Dow Chemical Co. Technology Acquisition Program is gratefully acknowledged. We would also like to thank Professor Thomas G. Spiro of Princeton University for helpful discussions.

Registry No. ZnTPP, 14074-80-7; ZnTPP$^{+}\cdot$, 39732-73-5; TPP, 917-23-7; TPP$^{+}\cdot$, 34479-64-6.

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Preparation and Structure of a Neodymium Complex Containing Bidentate (Carbamoylmethyl)phosphine Oxide Ligands

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Received April 25, 1985

Several groups have studied the metal ion extraction chemistry of bis(phosphine oxides).[1-3] Contrary to expectations it has been observed that with ligands of the type $R_2P(O)CH_2P(O)R_2$ replacement of alkyl groups, R, with phenyl groups, Ph, results in enhanced extraction ability at high acid concentrations for the phenyl-substituted bifunctional ligands. The so-called "aryl strengthening effect" has been rationalized in terms of an entropic stabilization in the extraction process;[1] however, a thorough understanding of the coordination chemistry of these ligands at the molecular level has not been obtained. In similar systems, Horwitz and co-workers[4] have found that replacement of alkoxy groups on (carbamoylmethyl)phosphonates (CMP's), $(RO)_2P(O)CH_2C(O)NR_2'$, with alkyl groups leads to larger liquid–liquid extraction coefficients ($K_D = [M_{org}]/[M_{aq}]$) for actinide ions.

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