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Catalysis of the Reduction of Molecular Oxygen to Water at Prussian Blue Modified Electrodes

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Abstract: The reduced form of Prussian blues, Prussian white, does have a catalytic activity for the reduction of molecular oxygen and of hydrogen peroxide in aqueous acidic electrolytes. Rotating ring–disk voltammetric measurements show clearly that the reduction product of molecular oxygen is not hydrogen peroxide but water produced by the four-electron-transfer reaction. The oxidized form of Prussian blues also acts as a catalyst for the oxidation of hydrogen peroxide. Two kinds of electron transfer channels in the Prussian blue crystal due to the redox reactions of the high-spin ions, $Fe^{3+/2+}$, and the low-spin iron ions, $Fe^{III/II}$, work as a catalyst for the reduction and oxidation of hydrogen peroxide, respectively. The results seem to demonstrate the importance of zeolitic natures and of metal centers in the crystal of Prussian blues.

The search for a relatively inexpensive catalyst/electrode combination for the electrochemical reduction of molecular oxygen (O_2) has received great interest because of the importance of fuel cells and air batteries.[1,2] The catalytic properties of metal phthalocyanines and porphyrins for this purpose have been most extensively examined.[3-6] Recently Collman et al. demonstrated the electrode catalytic activity of dicobalt "face-to-face" porphyrins.[6] The dicobalt cofacial porphyrin linked by four-atom bridges (the four-atom dimer) produced a catalyzed reduction almost exclusively to water. It has been pointed out that the O_2 reduction process was extremely sensitive to the geometry of the dimers. The five- and six-atom dimers were less potent than the four-atom dimer.[6b] The above results suggest clearly that each of two metal centers in a suitable geometry can transfer two electrons to an oxygen molecule, carrying out the four-electron process. The best situation for the reduction of O_2 seems to be that an oxygen molecule should be surrounded by either two- or four-electron sources. Such situations have been frequently discussed for cytochromes in living systems.[7]

Recently both the present authors and Neff have described the fundamental nature of Prussian blue (PB) and its relatives by means of electrochemistry.[8,9] The crystal structure of PB is a face-centered cubic lattice with a cell constant of 10.2 Å, indicating a very roomy crystal structure.[10] PB has been known as a zeolite with channel diameters of about 3.2 Å. Our previous study has demonstrated that only hydrated ions of K^+, Rb^+, Cs^+, and NH_4^+ can be expected to transport through the crystal of PB during the reduction of the high-spin iron ions, and experimental results agree completely with this expectation.[8c] From consideration of its size, the oxygen molecule should also be able to transport through the crystal of PB. The other important aspect of the structure of PB, $Fe_4^{3+}[Fe^{II}(CN)_6]_3 \cdot xH_2O$, with respect to the reduction of O_2, seems to be the positions of high-spin irons, Fe^{3+}, in the crystal (see Figure 1). The octant of the unit cell has four atoms of Fe^{3+} and $4 \times 3/4$ atoms of Fe^{II} at positions 4a and 4b, respectively.[10] The above circumstances strongly encouraged us to explore its potential application as a catalyst for the reduction of O_2. It can reasonably be expected that PB and its relatives have the capability of delivering two or four electrons, more or less simultaneously, to the O_2 molecule in the crystals. It has been briefly shown in our previous paper that an autoxidation of the reduced form of PB (Prussian white) to PB occurs in an oxygen-saturated solution.[8c] In this paper, it will be disclosed that the reduced form of PB, Prussian white, does have a catalytic activity for the reductions of O_2 and of hydrogen peroxide (H_2O_2) and, also, that the oxidized form of PB shows a catalytic activity for the oxidation of H_2O_2. Two kinds of electron-transfer channels in the PB crystal due to the redox reactions of the high-spin iron ions, $Fe^{3+/2+}$, and of the low-spin iron ions, $Fe^{III/II}$, work as a catalyst for the reduction and oxidation of H_2O_2, respectively. Cyclic voltammetry (CV) and a rotating ring–disk electrode (RRDE) were used for the experimental approach to be described.

Experimental Section

The PB films on glassy carbon (GC-20; Tokai Carbon Co.) electrodes were prepared in an aqueous ferric ferricyanide solution of an equal-volume mixture of 20 mM $FeCl_3$ and 20 mM $K_3Fe(CN)_6$ in 0.01 M HCl, as previously described.[8c] A large GC plate was used as a counter electrode. The electrodes were cathodically polarized in the above ferric ferricyanide solution by means of a galvanostatic condition where the current density was set between 3 and 50 $\mu A/cm^2$. Mainly, a current density of 5 $\mu A/cm^2$ was used. The electrodes, after the deposition of a certain amount of PB, were rinsed in 0.01 M HCl for 1 min. All the PB-modified electrodes were first examined in 1 M KCl (pH 3.0) under a nitrogen atmosphere by repeating the potential scan between 0.6 and –0.2 V where only the high-spin iron ions are involved in the electron-transfer reactions. After yielding steady voltammograms, they were subjected to further experiments as catalysts. During this potential excursion with the scan rate of 20 mV/s, the amount of PB deposits was measured by coulometry; the total amount of charge (Q_T) consumed by the reduction of the deposit was counted. The concentration of the hydrogen peroxide stock solution was determined by titration with standard potassium permanganate.[11] All chemicals were of analytical

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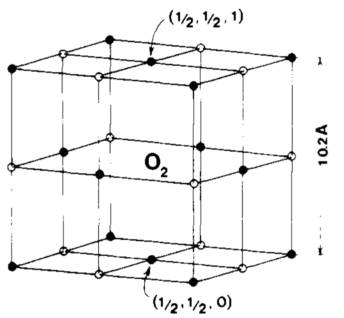

Figure 1. Illustrative depiction of the unit cell of Prussian blue ($Fe_4^{3+}[Fe^{II}(CN)_6]_3 \cdot xH_2O$). Water molecules ($xH_2O$) and cyanide ions are omitted. (●, Fe^{3+}, ○, Fe^{II}.)

grade, and solutions were prepared with water that was deionized and then distilled twice in an all-glass still.

Rotating GC disk electrodes used have been described previously.[8e] For the ring–disk electrode measurements, the disk was made of GC (diameter 0.30 cm) with platinum as the ring (inner diameter 0.33 cm). The assembly was airtight and used Teflon rods as spacers. The ring–disk electrode was calibrated with the ferrocyanide/ferricyanide couple, yielding a collection efficiency, N, of about 0.15. The PB film was prepared only on the surface of the GC disk electrode by the electrochemical method described above. During the electrochemical preparation of the PB film on the disk electrode, deposition of a small amount of PB (less than 3 mC/cm^2) was not avoided on the Pt ring electrode because of the chemical deposition of PB as described previously.[8c] However, the PB films on the ring electrode were completely swept out by repeating the electrode potential scan of the ring electrode between the potentials where hydrogen and oxygen evolution was observed. Because the ring electrode was used for the detection of intermediate (H_2O_2) in the course of the reduction of O_2, the small amount of PB on the ring electrode did not affect the experimental results obtained by RRDE, even if PB was present on the Pt ring. It is well-known that the current response of Pt electrodes toward H_2O_2 oxidation shows a gradual loss of potency.[5a] However, it will be shown in this paper that PB-modified electrodes have a high catalytic activity for hydrogen peroxide, not only for reduction but also for oxidation. An electrode rotator (Nikko-RRD-1) was used. Voltammograms were obtained with PAR (Princeton Applied Research) Model 174 instruments equipped with a Model 179 digital coulometer. A saturated calomel electrode (SCE) was used as the reference electrode. The catalytic activities of the PB-modified GC electrode were examined in the solutions of 1 M KCl and of 0.5 M K_2SO_4 whose pH values were adjusted by HCl and H_2SO_4, respectively. Experiments were conducted at a temperature of 20 (±1) °C.

Results and Discussion

Catalyzed Molecular Oxygen Reduction. Figure 2A shows the cyclic voltammogram of a PB-modified GC electrode in 1 M KCl (pH 3.0) under a nitrogen atmosphere. The film of PB was prepared at a low current density of 5 μA/cm^2. The shape of the voltammogram is typical for the films prepared at lower current densities (<10 μA/cm^2), although it depends on the current density used for the electrochemical preparation method described previously.[8c] When current densities more than 10 μA/cm^2 were employed in the ferric ferricyanide solution of an equal-volume mixture of 20 mM $FeCl_3$ and 20 mM $K_3Fe(CN)_6$, very sharp spikes were recorded for the electron-transfer reactions of the high-spin iron ions in the PB film.[8c] It has been conclusively shown by an in situ Mössbauer measurement that the reduction and the oxidation waves of PB observed at 0.2 and 0.9 V vs. SCE are due to the electron-transfer reactions of the high-spin iron ions and of the low-spin iron ions in the film, respectively.[8d]

The wave at 0.2 V has been formulated as follows, assuming that the formula of PB is the water insoluble one,

$$Fe_4^{3+}[Fe^{II}(CN)_6]_3 \cdot xH_2O + 4e^- + 4K^+ \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} K_4^+Fe_4^{2+}[Fe^{II}(CN)_6]_3 \cdot xH_2O \quad (1)$$

where Fe^{3+}, Fe^{II}, and K^+ are the high-spin iron ion, the low-spin iron ion, and the potassium ion, respectively.

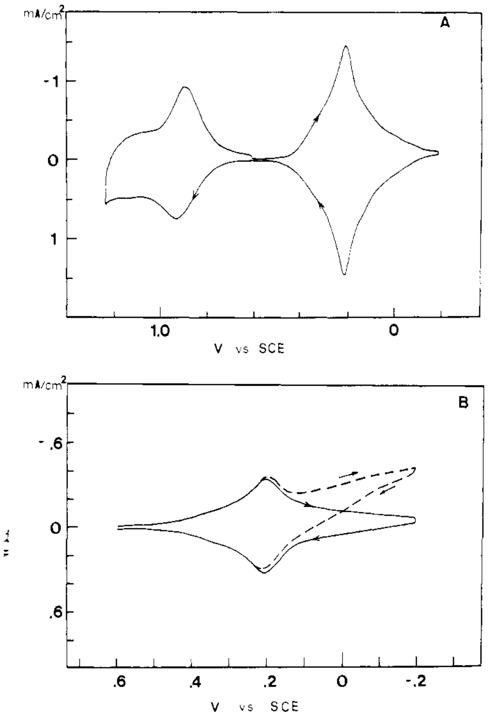

Figure 2. (A) Cyclic voltammogram of a PB-modified GC electrode with 6 mC/cm^2 of PB at a scan rate of 50 mV/s in the absence of O_2. (B) Cyclic voltammograms of a rotating PB-modified electrode with 4.2 mC/cm^2 of PB in the absence (solid line) and in the presence of O_2 (saturated) (dashed line). The electrode was rotated at 1000 rpm. The potential was scanned at 20 mV/s. The supporting electrolyte was 1 M KCl (pH 3.0).

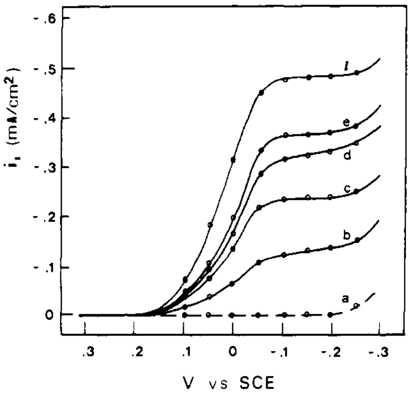

Figure 3. Current–potential curves for the reduction of O_2 at a bare GC disk (dashed line (a)) and at PB-modified electrodes with the following amounts of PB, 2 (b), 2.8 (c), 4.2 (d), 4.8 (e), and 6 mC/cm^2 (f), in O_2-saturated solution. Supporting electrolyte: 1 M KCl (pH 3.0); electrode rotating speed 1000 rpm.

Figure 2B shows the cyclic voltammograms for the reduction of O_2 at a PB-modified GC electrode. The solid line shows the voltammogram only for the electron-transfer reaction of the high-spin iron ions in PB under a nitrogen atmosphere, the same as that in Figure 2A. On the other hand, a fairly large increase in the cathodic current is found in an oxygen-saturated solution, as shown by a dashed line in Figure 2B. The reduction of oxygen seems to commence at about 0.2 V vs. SCE where about a half of the trivalent high-spin iron ions, Fe^{3+}, are reduced to Fe^{2+}. The correspondence between the electrode potential for the reduction of oxygen and that of PB strongly suggests that the high-spin iron ions in PB have catalytic activity and should be involved in the reduction of oxygen.

In order to separate the reduction process of oxygen from the waves of PB itself, we employed steady-state measurements at the rotating disk GC electrode. The reduction currents for oxygen

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with and without the PB film at a particular rotation speed (1000 rpm) in an oxygen-saturated 1 M KCl solution (pH 3.0) are shown in Figure 3. The currents were measured point by point by waiting (for about 10 s) at each potential until it became steady.

At the bare GC electrode, the reduction of oxygen commences at about −0.25 V vs. SCE (dashed line). Almost no current is found at the bare electrode at potentials more positive than −0.2 V. However, the catalyzed reduction currents start at about 0.2 V vs. SCE at the PB-modified electrodes. It is obvious that the current is strongly enhanced and that the overpotential is reduced by about 400 mV or even more when oxygen is reduced at the PB-modified electrodes.

The catalyzed reduction currents are increased by increasing the amount of PB. The dependence of the magnitude of the current on the amount of the catalyst is almost linear in the range examined here (see also Figure 8 later in the paper). This plainly demonstrated that the oxygen reduction takes place inside the PB lattice in which both O_2 molecules and the products are able to diffuse rapidly enough to sustain the measured current. In our previous paper,[8e] it has been clearly shown that the reactants such as $Fe^{II}(CN)_6^{4-}$, $IrCl_6^{2-}$, and $Ru^{III}(edta)$ in the solution can undergo the mediated electron-transfer reactions with the redox centers in the PB films only at the interface between the solution and the PB films. That is, the above redox species cannot be expected to transport through the crystal of PB due to their massive size. In contrast, one can expect that an oxygen molecule will be able to go in and out of the crystal of PB because of its molecular size.

As may be seen from the comparison of the dashed line and the solid lines in Figure 3, the second increase in the reduction of oxygen is found at −0.2 V vs. SCE, at the PB-modified electrodes where the reduction of oxygen seems just to commence at the bare GC electrode. This further increase in the current observed at the PB-modified electrodes can be ascribed to the reduction of oxygen at the interface between the PB film and the GC electrode. Unreacted oxygen molecules diffuse through the crystal of PB and then can be reduced at the surface of the GC electrode. As discussed above, molecules of oxygen may be expected to diffuse in and out of the crystal of PB. If this was not the case, one could not expect that the reduction of oxygen would increase further at −0.25 V and increase with increases in the amount of catalyst.

Note that the catalytic activity of PB toward O_2 reduction depended on the rate of film growth, i.e., the current density used for the preparation of the PB films. The general trend was that the lower the current used for the preparation of the film was, the more the activity achieved. The ratio of the catalyzed limiting current (i_L) to the amount of PB was about 0.8 mA/10 mC at a rotation speed of 1000 rpm when the PB films were prepared at a current density less than 5 $\mu A/cm^2$. The ratio was about 0.4 mA/10 mC when a current density of 20 $\mu A/cm^2$ was used. However, the catalyzed currents were very easy to reproduce as long as a constant current density was applied. For this reason, a current density of 5 $\mu A/cm^2$ was mainly used in the present study. It has been pointed out in our previous study that the voltammograms of PB-modified electrodes strongly depend on the current density used for the preparation of the PB film.[8c] A very sharp spike was measured for films prepared at higher current densities. We have proposed that uncoordinated $Fe(CN)_6^{3-/4-}$ or $Fe^{3+/2+}$ ions, which are occluded in lattice defects produced at higher current densities, are the reason for the current spike.[8c] It is very possible that such uncoordinated ions may decrease the number of reaction sites in the film where O_2 can be reduced.

For the studies of oxygen reduction, the technique of rotating ring–disk voltammetry has been extensively used by many authors.[5,6,12-14] The principle has been simply described by Anson et al.[6b] A platinum ring electrode held at a potential of 1.2 V vs. SCE was used for the detection of any hydrogen peroxide formed at the disk.[6b] Figure 4 shows typical ring–disk voltammetric results obtained at a rotation speed of 1000 rpm. At the bare GC disk electrode (dashed line), the anodic current observed at the Pt ring electrode strictly shows that the dominant reduction product is hydrogen peroxide, as previously described.[12] However, an extremely important difference can be seen in the reduction of oxygen, at all potentials, at the PB-modified electrodes (solid lines). No detectable amount of anodic ring current was measured at any of the potentials used here. Even if the sensitivity of the instrument for the ring current was considerably increased and the highest rotation speed (10^4 rpm) was employed, no ring current was observed. This results is a clear evidence that the reduction product is not hydrogen peroxide, but water produced by the four-electron reduction of oxygen.

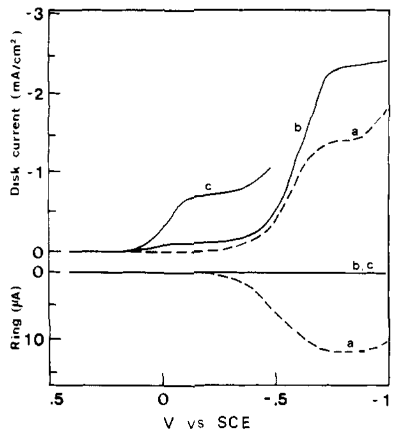

Figure 4. Ring–disk current–potential curves for the reduction of O_2 at a bare GC disk (dashed line (a)) and at a PB-modified GC disk with the following amounts of PB, 1.4 (b) and 8.5 mC/cm² (c), in 0.5 M K_2SO_4 (pH 3.0; O_2 saturated) at a rotating speed of 1000 rpm. The ring potential was held at 1.2 V vs. SCE.

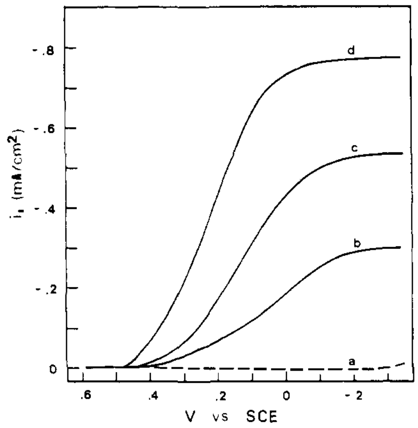

Figure 5. Current–potential curves for the reduction of H_2O_2 (0.4 mM) at a bare GC disk (dashed line(a)) and at a PB-modified GC disk with the following amounts of PB, 0.8 (b), 1.3 (c), and 6.9 mC/cm² (d), in 1 M KCl (pH 3.0; nitrogen saturated) at a rotating speed of 1000 rpm.

The reduction currents observed at the disk electrodes in the potential range from 0.2 to −0.25 V are reasonably ascribed to the catalyzed reduction of oxygen at the PB-modified electrodes, but the further increase in currents commencing at −0.25 V is due to a different origin, that is, the oxygen molecules passing through the PB lattice start to be reduced at the surface of the GC electrode as expected above. The nonappearance of anodic current at the ring electrode at disk electrode potentials more negative than −0.25 V indicates strongly that the reduced form of PB also has catalytic activity for the reduction of hydrogen peroxide because hydrogen peroxide is the dominant product at the bare GC electrode as shown in Figure 4. It is noteworthy that the height of the second plateau observed at a GC electrode with a thin PB film (1.4 mC/cm²) is much larger than that observed at the bare GC

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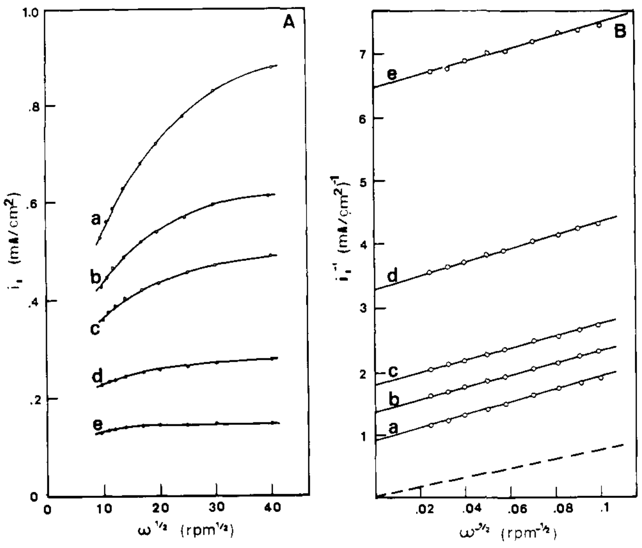

Figure 6. Limiting current vs. (rotating speed)$^{1/2}$ (A) and Koutecky–Levich plots (B) for the reduction of O_2 at PB-modified electrodes with the following amounts of PB, 8.5 (a), 6.3 (b), 4.3 (c), 3.1 (d), and 1.3 mC/cm^2 (e), in 1 M KCl (pH 3.0; O_2 saturated). The electrode potential was held at −0.15 V vs. SCE. The dashed line shows the calculated slope for the four-electron reduction of O_2.

Table I. Kinetic Parameters for the Reduction of O_2 Catalyzed by the Films of Prussian Blue in 1 M KCl (pH 3.0)

solutions (C_{O_2})	$\Gamma_{Fe^{3+}}$,[a] mC/cm^2	Γ_{PB},[b] mol/cm^2	i_{kin},[c] mA/cm^2	k_{O_2},[d] M^{-1}s^{-1}
O_2 saturated (1.15 mM)	1.4	3.6×10^{-9}	0.156	0.97×10^2
	3.1	8.1×10^{-9}	0.30	0.78×10^2
	4.3	1.1×10^{-8}	0.55	1.11×10^2
	6.3	1.64×10^{-8}	0.72	1.0×10^2
	8.5	2.2×10^{-8}	1.11	1.14×10^2
air saturated (0.24 mM)	3.3	8.6×10^{-9}	0.082	1.07×10^2
	4.8	1.2×10^{-8}	0.124	1.1×10^2

[a] Amount of the high-spin iron ions. [b] Concentration of the unit cell. [c] Kinetic current. [d] Rate constants calculated by $i_{kin} = 4Fk_{O_2}\Gamma_{PB}C_{O_2}$.

electrode. The explanation for this is that once hydrogen peroxide is formed at the GC surface in the PB-modified electrode, its reduction to water proceeds rapidly.

Catalyzed Hydrogen Peroxide Reduction. Typical current–potential curves for the reduction of hydrogen peroxide at rotating PB-modified GC disk electrodes are shown in Figure 5. The reduction of hydrogen peroxide at bare GC electrode occurs at much more negative potentials than for PB-modified electrodes. Apparently the catalyzed reduction of hydrogen peroxide commences at about 0.5 V vs. SCE, where the reduction of the trivalent high-spin iron ions, Fe^{3+}, in the film has just started. This behavior positively suggests that the reduction of hydrogen peroxide is really catalyzed by the divalent iron ion, Fe^{2+}, centers in the PB film. The catalyzed reduction currents are increased by increasing the amount of PB just as observed in the course of the reduction of oxygen shown in Figure 3. This result suggests that not only oxygen molecules but also hydrogen peroxide would be able to diffuse through the crystal of PB. At GC electrodes with more than 10 mC/cm^2 of PB film, the limiting currents are nearly equal to the mass transfer limited Levich currents corresponding to the rapid two-electron reduction of hydrogen peroxide. Comparing the current–potential curves shown in Figures 3 and 5, one could expect that the rate of the catalyzed reduction of hydrogen peroxide to water would be faster than that of oxygen.

Kinetics of Reactions at PB-Modified Electrodes. For the simple reaction, at rotating disk electrodes,

$$\mathrm{Ox} + ne \rightleftharpoons \mathrm{Red} \tag{2}$$

the limiting current (i_{lev}) is expressed by the Levich equation[15]

$$i_{lev} = 1.554nFAD^{2/3}\nu^{-1/6}C_0\omega^{1/2} \tag{3}$$

where D, ν, C_0, and ω are the diffusion coefficient, the kinematic viscosity, the bulk concentration, of the reactant in the solution, and the rotation speed in Hertz, respectively.

The detailed description of the kinetic process at the modified electrodes has been comprehensively treated by Andrieux et al.[16] When the catalyzed reaction is only limited by the rate of the electron-transfer reaction between the reactants in the solution and the redox centers in the PB film, the limiting current (i_L) for the catalyzed reaction, which is not entirely transport controlled, can be expressed by the Koutecky–Levich equation

$$1/i_L = 1/i_{lev} + 1/i_{kin} \tag{4}$$

The kinetic current, i_{kin}, is assumed to obey eq 5,

$$i_{kin} = (n \times 10^3)k\Gamma_{PB}FC_0 \tag{5}$$

where i_{kin} is the kinetic current density, k the rate constant for the catalyzed reaction (M^{-1}s^{-1}), Γ_{PB} the concentration of unit cells in the PB film on the electrode surface (mol cm^{-2}), F the Faraday constant, and C_0 the concentration of the reactants (mol cm^{-3}).

Figure 6A shows the observed limiting current (i_L) vs. rotation speed data for the reduction of O_2 obtained at −0.15 V vs. SCE in an oxygen-saturated solution. These data indicate clearly that the limiting currents observed at PB-modified electrodes are not entirely transport controlled but are also controlled by the catalytic electron-transer kinetics. The variation of the limiting currents with rotation speed is plotted in Figure 6B according to the Koutecky–Levich equation. The expected linearity was obtained. The slopes of the plots shown in Figure 6B are all close to the calculated slope for the four-electron reduction ($n = 4$) of oxygen (dashed line). For the calculation of the slope, the following values were used: the kinematic viscosity, ν, was 0.01 cm s^{-1};[13] the diffusion coefficient, D was 2.0×10^{-5} cm^{2}s^{-1};[4b] and the concentration of oxygen in the oxygen-saturated solution, C_{O_2}, was 1.15×10^{-3} M.[4b] Note that the calculated slope for the four-electron reduction is lower than that obtained for PB films. The number of electrons, n is estimated as about 3 on the basis of the values of the experimental slope. However, this might be due to a surface roughness of the PB films. We believe that the correspondence of the experimental and calculated slopes seems to be an evidence that PB films are able to reduce oxygen to water.

From the intercepts of Figure 6B, which correspond to infinite rotation speed, the rate constant for the catalyzed reduction of oxygen was evaluated. Exactly the same experiment has been carried out in air-saturated solutions. Note that the slopes and intercepts of the Koutecky–Levich plots differ by a factor of 5 in oxygen- and air-saturated solutions, indicating that the catalyzed reaction is first order with respect to the concentration of oxygen. The data are summarized in Table I. The rate constants evaluated from the Koutecky–Levich equation seem to be independent of the bulk concentration of oxygen in the solution and of the surface concentration of PB. These results are expected from eq 5.

This independence shows conclusively that oxygen molecules are able to diffuse rapidly through the crystal of PB and are reduced to water in the crystal. In the case of the porphyrin catalysts, it has been pointed out by Anson et al. that additional catalyst more than several equivalent monolayers thick does not produce a further increase in the current, indicating that oxygen molecules cannot diffuse through the layers of porphyrins.[5b] However, as noted in our previous paper, the measured thickness of the PB film was about 2000 Å for a charge density of 10 mC/cm^2.[8e] This value is only slightly larger than the calculated value (1655 Å) for a (100) face of the single crystal of PB with a cell constant of 10.2 Å (see Figure 1). The film with a charge density of 10 mC/cm^2 has about 162 layers of the unit cell of PB.

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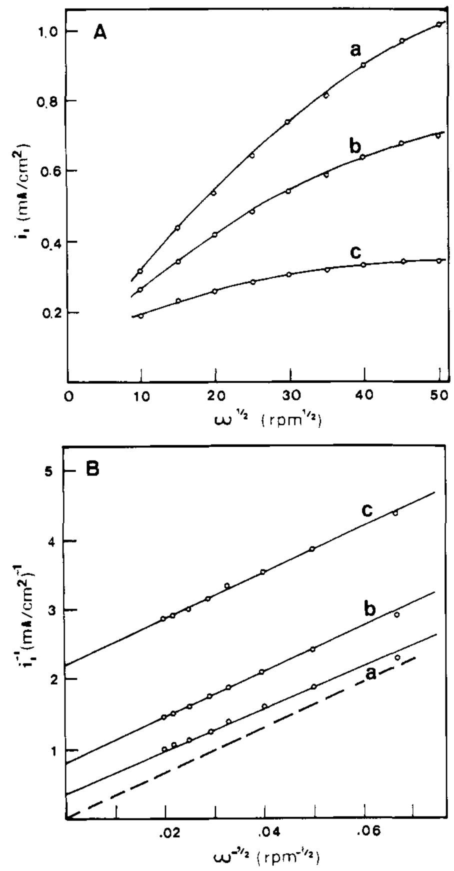

Figure 7. Limiting current vs. (rotating speed)$^{1/2}$ (A) and Koutecky–Levich plots (B) for the reduction of H_2O_2 (0.4 mM) at PB-modified electrodes with the following amounts of PB, 6.9 (a), 1.3 (b), and 0.8 mC/cm^2 (c), in 1 M KCl (pH 3.0; nitrogen saturated). The electrode potential was held at −0.15 V vs. SCE. The dashed line shows the calculated slope for the two-electron reduction of H_2O_2.

Table II. Kinetic Parameters for the Reduction of H_2O_2 by the Films of Prussian Blue in 1 M KCl (pH 3.0)

concn, mM	$\Gamma_{Fe^{3+}}$, mC/cm^2	Γ_{PB}, mol/cm^2	i_{kin}, mA/cm^2	$k_{H_2O_2}$,^{a} M^{-1} s^{-1}
0.4	0.8	2.1×10^{-9}	0.45	2.8×10^3
	1.3	3.4×10^{-9}	1.3	5×10^3
	6.9	1.8×10^{-8}	2.8	2.0×10^3
0.2	1.7	4.4×10^{-9}	0.93	5.5×10^3
	3.5	9.1×10^{-9}	2.1	6×10^3
	5.2	1.35×10^{-8}	2.7	5.2×10^3

^{a}Rate constants calculated by $i_{kin} = 2Fk_{H_2O_2}\Gamma_{PB}C_{H_2O_2}$.

We would particularly like to stress that the zeolitic nature of PB with channel diameters of about 3.2 Å should be extremely important for the diffusion of oxygen molecules through the crystal. Without such channels, PB would not be expected to act as a catalyst for oxygen reduction. Therefore, we conclude that the PB films do act as a *three-dimensional catalyst*. It is well-known that many zeolites used as catalysts have specific channel diameters for a particular reaction.[20]

Figure 7A shows typical Levich plots obtained in the nitrogen-saturated solution of H_2O_2 (0.4 mM). It is again found that the limiting currents for the reduction of H_2O_2 at PB-modified electrodes are not entirely transport controlled but are also partially controlled by the catalyzed electron-transfer kinetics. The Koutecky–Levich plots shown in Figure 7B yield a good linearity expected from eq 4. The slopes of the lines are the same within experimental error as that expected for $n = 2$. For the calculation of the theoretical slope, the diffusion coefficient of H_2O_2 is taken as 6.8×10^{-6} cm^2/s.[4b,18] The correspondence between the theoretical and the measured slopes proves that the divalent iron ions, Fe^{2+}, in PB really are a catalyst for the reduction of H_2O_2 ($n = 2$), not for decomposition such as the disproportionation of H_2O_2 to O_2.

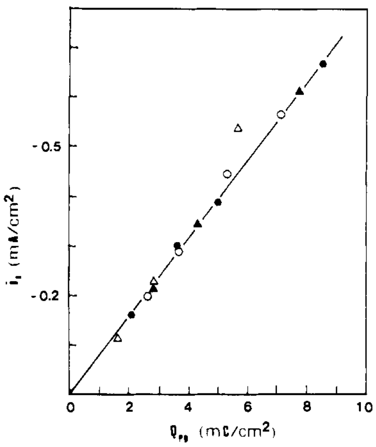

Figure 8. Catalyzed limiting current for the reduction of O_2 as a function of pH. The electrode was rotated at 1000 rpm. The supporting electrolyte was 1 M KCl. The pH values were as follows: (▲) 4.0, (○) 3.0, (●) 2.0, and (△) 1.0. Q_{PB} is the amount of PB.

The rate constants, $k_{H_2O_2}$, are summarized in Table II. The evaluated rate constants are almost independent of the bulk concentration of H_2O_2 and of the surface concentration of PB, just as in the reduction of oxygen. The rate constants for the catalyzed reduction of H_2O_2 are about 20 times larger than that of k_{O_2}. Forshey and Kuwana have recently reported a value of 2.5×10^5 M^{-1} s^{-1} for the reaction of iron (Fe^{2+}) tetrakis(*N*-methyl-4-pyridyl)porphyrin and H_2O_2.[4b] Shigehara and Anson found a value of 8.6×10^3 M^{-1} s^{-1} at coatings of a Ru(III)–polymer complex.[12]

pH Dependence. The waves for the PB-modified electrodes in oxygen-free solutions are not affected considerably by the pH (1.5–7), as long as the solution contains an excess of potassium chloride as a supporting electrolyte. Although the shape of the waves at 0.2 V vs. SCE was slightly changed by changing the pH of the solution, the peak potentials were almost the same as reported by Neff et al.[9b] However, the catalytic activities of the PB-modified electrodes are independent of the pH values of 1 M KCl as shown in Figure 8. The lack of pH dependency of the catalytic activity and of the peak potentials of the PB films suggests that the proton concentration in the crystal of PB would not be affected by the concentration of protons in the bulk solution. Therefore, it can be considered that the consumption of protons by the reduction of O_2 and H_2O_2 might be compensated by the proton jumping from the solution into the PB crystal, because about 14–16 molecules of water (per unit cell) exist in the crystal, as pointed out by Ludi et al.[10] It is noteworthy that the waves of the PB-modified electrodes in a 0.1 M HCl solution without KCl were easily destroyed after a few scans from 0.6 to −0.2 V, as previously reported.[8c] This results suggests that the PB film is not stable when only protons are injected excessively into the crystal in order to maintain the charge balance.

The PB film is gradually disintegrated by hydrolysis in the solutions with pH values above 7, as previously reported. Therefore, the utility of PB-modified electrodes for the reduction of oxygen is eventually limited in acidic solutions.

The Mechanism of Catalyzed Reductions. Figure 1 illustrates the unit cell of PB. It should be pointed out regarding the reaction sites that Ludi et al. have reported a detailed neutron diffraction study of PB, indicating the existence of two structurally distinguishable kinds of water molecules.[10] The vacancies of the low-spin

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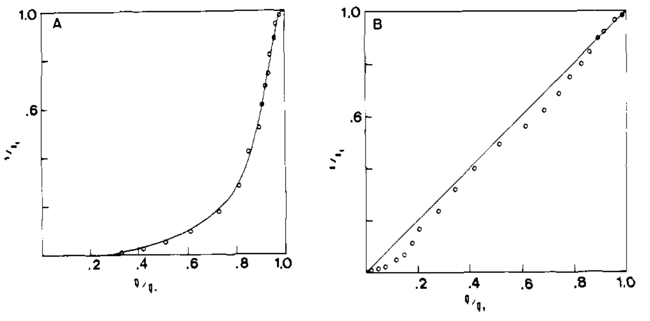

Figure 9. Relationship of the catalyzed O_2 (A) and the catalyzed H_2O_2 reductions (B) to the degree of the reduction of PB (Q/Q_T). Q_T is the total amount of charge consumed by the reduction of the deposit.

iron ions, $Fe^{II}(CN)_6$, distributed randomly cause six coordinated water molecules to complete the pseudooctahedral coordination of Fe^{3+}, with about eight uncoordinated water molecules in the unit cell.[10] Water molecules are omitted for the sake of clarity in Figure 1. It is quite possible that such vacancies take an important role in the course of reductions of oxygen and H_2O_2 in the crystal of PB. When an oxygen molecule locates in the center of each vacancy, the molecule will be surrounded by four divalent high-spin iron ions on average, in the reduced form of PB. One of two possible pathways is that an oxygen molecule receives simultaneously four electrons, leading to two water molecules.

$$O_2 + 4H^+ + K_4^+Fe_4^{2+}[Fe^{II}(CN)_6]_3\cdot xH_2O \rightarrow Fe_4^{3+}[Fe^{II}(CN)_6]_3\cdot xH_2O + 2H_2O + 4K^+ \qquad (6)$$

$$+4e^-$$

The other is a mechanism involving oxygen reduction through hydrogen peroxide in a series pathway, i.e., the "2 + 2 mechanism",[4b]

$$O_2 + 2H^+ + K_4^+Fe_4^{2+}[Fe^{II}(CN)_6]_3\cdot xH_2O \rightarrow K_2^+Fe_2^{3+}Fe_2^{2+}[Fe^{II}(CN)_6]_3\cdot xH_2O\cdot H_2O_2 + 2K^+ \qquad (7)$$

$$2H^+ + K_2^+Fe_2^{3+}Fe_2^{2+}[Fe^{II}(CN)_6]_3\cdot xH_2O\cdot H_2O_2 \rightarrow Fe_4^{3+}[Fe^{II}(CN)_6]_3\cdot xH_2O + 2K^+ + 2H_2O \qquad (8)$$

where H_2O_2 indicates the hydrogen peroxide presented in the crystal. We believe that H_2O_2 may be an important species in the system described here. The nonappearance of H_2O_2 in the rotating-disk experiment shown in Figure 4 can be explained by supposing that all of the H_2O_2 formed as an intermediate is completely reduced to H_2O in the crystal before diffusion out of the crystal of PB takes place.

Further interesting results are shown in Figure 9. These plots indicate the dependence of the reactivities of the reduced form of PB toward oxygen and H_2O_2 on the degree of reduction of PB. In the case of oxygen reduction, partially reduced forms of PB do not have an appreciable reactivity as long as the degree of the reduction (Q/Q_T) is less than 0.25. It can be assumed that only one of the four trivalent high-spin iron ions is reduced to be divalent in a unit cell on average, at one-fourth reduction ($Q/Q_T = 0.25$). In this circumstance, the probability of taking up two electrons simultaneously seems to be so small that one-fourth reduced PB is almost totally inactive for the reduction of oxygen. The catalyzed reduction current of oxygen starts practically at degrees of reduction of PB more than 0.25. However, the catalyzed currents reach a plateau at about −0.05 V vs. SCE, where more than 85% of the trivalent high-spin iron ions are reduced to Fe^{2+}. In other words, the highest activity can be achieved by the fully reduced form of PB, not by partially reduced forms. The above results suggest that the first two-electron process (eq 7) is a rate-determining step for the reduction of oxygen. From a geometrical point of view, at least two of the four Fe^{3+} ions must be reduced to Fe^{2+} ions for the two-electron reduction process yielding H_2O_2. Although one can expect that the above situation holds at the potential of 0.2 V vs. SCE, the catalyzed current is still about 10% of the limiting value. This result requires a further consideration of the actual positions of the high-spin iron ions surrounding oxygen molecules. If the two Fe^{2+} ions are located at the positions ($^1/_2$, $^1/_2$, 0) and ($^1/_2$, $^1/_2$, 1), the distance (10.2 Å) between two iron ions appear to be too large to deliver two electrons simultaneously to an oxygen molecule. If this is true, a pair of positions of the nearest neighbors must be reduced. The result shown in Figure 9A may be explained from these statistical considerations.

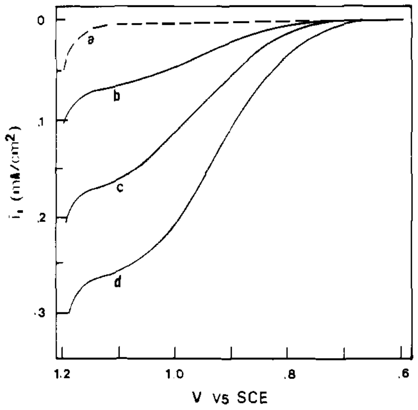

Figure 10. Current–potential curves for the oxidation of H_2O_2 (0.4 mM) at a bare GC disk (dashed line(*a*)) and at a PB-modified GC disk with the following amounts of PB, 1.3 (b), 3.4 (c), and 12.8 mC/cm^2 (d), in 1 M KCl (pH 3.0; nitrogen saturated) at a rotating speed of 1000 rpm.

In contrast with the result for the reduction of oxygen, an almost linear dependence is found for the reduction of H_2O_2, as shown in Figure 9B. In the case of the reduction of H_2O_2, it does not matter in which positions the Fe^{2+} ions are located. The catalyzed currents depend only on the amount of Fe^{2+} ions in the crystal.

Catalyzed Hydrogen Peroxide Oxidation. Figure 10 demonstrates clearly that PB-modified electrodes do also have catalytic activity for the oxidation of H_2O_2. The half-wave potentials of the catalyzed oxidation waves are about 0.9 V vs. SCE. In a similar manner to the reduction of H_2O_2, the oxidation of H_2O_2 does not show a clear wave at a bare GC electrode. Only a small shoulder was observed at potentials where large background anodic currents commenced. However, the catalyzed oxidation of H_2O_2 commences at a potential of about 0.7 V vs. SCE where the low-spin iron ions, Fe^{II}, are oxidized to Fe^{III} as shown in Figure 2. This correspondence in the potential supports strongly the view that the trivalent low-spin iron ions do act as catalyst for the oxidation of H_2O_2. A detailed investigation has been carried out with use of the rotating-disk electrode. The limiting current vs. rotation speed data indicated that the oxidation of H_2O_2 was not transport controlled but controlled by the catalytic kinetics just as in the reduction of H_2O_2. From the Koutecky–Levich plots, which were perfectly straight lines, a rate constant of about 4×10^2 M^{-1} s^{-1} was evaluated as an average value while changing the concentration of H_2O_2 (in the range of 0.5 to 2.5 mM) and the amount of PB (in the range 1 to 7 mC/cm^2). The value obtained was obviously smaller than that for the reduction of H_2O_2.

Mercury electrodes are well-known to respond reversibly to the oxygen–hydrogen peroxide couple in an alkali solution.[17] Durand and Anson have recently reported that a cobalt(II) porphyrin catalyzes the oxidation of H_2O_2.[5a] They found a value of 6×10^4 M^{-1} s^{-1} in a solution of pH 12. However, it was also pointed out that the catalyst appeared to lose its potency to catalyze the oxidation at lower pH values than 12. For the above reason, the measurements of the rate constants were limited to pH 12 or higher for cobalt(II) porphyrin.[5a] An anodic oxidation wave for H_2O_2 at a platinum electrode appeared with a half-wave potential of about 0.95 V vs. SCE. However, the current response of the bare platinum electrode toward H_2O_2 oxidation was severely affected by its pretreatment and showed a gradual loss of potency. The same behavior has been found by Anson et al.[5a] On the other hand, the catalyzed oxidation currents were reproduceable at the PB-modified electrodes.

Eventually, we conclude that the oxidized form of PB is one of the best catalysts toward H_2O_2 oxidation in acidic solutions. It is reasonable to believe that the catalyzed oxidation of H_2O_2 proceeds in crystals of the oxidized form of PB just as expected for the reduction of H_2O_2, because the catalyzed oxidation also showed first-order dependence on the concentrations of H_2O_2 and Γ_{PB}.

It is noteworthy that the stability of the catalyst represented here was excellent under certain conditions. The stability of the wave of PB itself was extremely high as described in our previous papers.[8] For this reason, the PB-modified electrode can be applied in an electrochromic display device.[8a] Toward O_2 reduction, a lifetime experiment showed that only a few percent decrease in the catalyzed current was observed after 30 h holding the electrode potential at -0.2 V vs. SCE. Such a high durability should be important for its application such as fuel cells and air batteries. However, we found a gradual loss in activity when a large amount of PB (20 mC/cm^2) was employed in order to obtain higher current densities. When observed under a microscope, the film of PB was sometimes partially removed. This behavior may be explained by poor adhesion of the PB film on the GC surface.

Finally, we briefly mention Prussian blue analogues. It has already been shown that iron–ruthenium cyanide (ruthenium purple; RP), $Fe_4^{3+}[Ru^{II}(CN)_6]_3$, and iron–osmium cyanide, $Fe_4^{3+}[Os^{II}(CN)_6]_3$, can be prepared by an electrochemical method.[19] It was found that both were active for the reduction of O_2. Applications as catalysts can be readily expected from the above results.

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Registry No. Fe, 7439-89-6; O_2, 7782-44-7; H_2O_2, 7722-84-1; H_2O, 7732-18-5; C, 7440-44-0; PB, 12240-15-2; Prussian white, 81681-39-2.

Structure of C_{3v} P horanyl and C_{4v} Phosphorane Anion Radicals. A Qua Chemical Study

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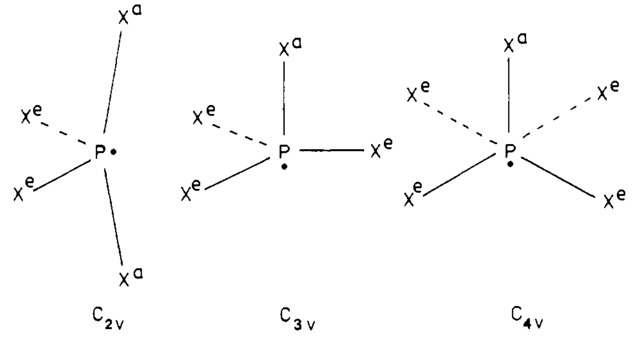
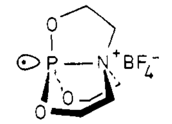
Abstract: Ab initio molecular orbital calculations on various C_{3v} phosphoranyl radicals and the C_{4v} $\dot{P}F_5^-$ phosphorane anion radical are presented. By the unrestricted Hartree–Fock method with a 4-31G basis set the geometries for C_{3v} $X^a\dot{P}X^e_3$ (X^a = apical ligand, X^e = equatorial ligand) radicals were optimized for X = H, F, and Cl. All C_{3v} radicals reveal a trigonal-bipyrimidal structure with the unpaired electron in apical position. The optimized $\dot{P}F_5^-$ radical is octahedral with the unpaired electron acting as a ligand. The calculated isotropic hyperfine coupling constants are in good agreement with the experimental values. Variation of the apical–equatorial bond angle for $H\dot{P}H_3$ and $\dot{P}F_5^-$ leads to σ^*-arrangements. A detailed study of the C_{3v} PH_3 + H· potential energy surface is described. It appears that a σ^*-arrangement is not stable but leads to dissociation. The stability of $X^a\dot{P}H_3$ with respect to dissociation into PH_3 and X^a· is described, and transition states are calculated. $H\dot{P}H_3$ lies 43.2 kJ mol^{-1} below its transition state, $F\dot{P}H_3$ (9.8 kJ mol^{-1}), whereas $Cl\dot{P}H_3$ is unstable.

I. Introduction

A number of single-crystal ESR studies have shown that phosphoranyl radicals ($\dot{P}X_4$) can adopt different configurations depending on the ligands attached to phosphorus and steric constraints of ring structures.[1-4] Most frequently a C_{2v} geometry is encountered. The electronic structure of these C_{2v} phosphoranyl radicals is well established and may be described as a trigonal bipyramid (TBP) with the unpaired electron acting as a fifth ligand in an equatorial position.[2,5-7] In contrast to the structure of C_{2v} phosphoranyl radicals, conflicting ideas exist on the electronic structure of phosphoranyl radicals with a C_{3v} geometry and phosphorane anion radicals with a C_{4v} geometry. The unpaired electron in the $Ph_3\dot{P}Cl$ radical, which possesses a C_{3v} geometry, is believed to reside in a σ^* P–Cl orbital,[3] accounting for the high spin density found on chlorine and the fact that the ^{31}P tensor is parallel to the ^{35}Cl tensor. By contrast the extensive studies on the C_{3v} radical $\cdot\overline{P(OCH_2CH_2)_3N}^+BF_4^-$ show unambiguously





that the unpaired electron resides in the apical position of a TBP (TBP-a).[1,8] The near isotropic ^{14}N hyperfine coupling of 22 G

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