$$j = \frac{i\hbar}{4\pi m} \left\{ \psi \frac{\partial \psi^*}{\partial x} - \psi^* \frac{\partial \psi}{\partial x} \right\}$$
(22)

Using the wave functions  $\psi_i$ ,  $\psi_r$ , and  $\psi_t$  in eq 17 and 18, we calculated from eq 22 the corresponding incident, reflected, and transmitted fluxes,  $j_i$ ,  $j_r$ , and  $j_t$ . The results are displayed in Figure The ratios  $|j_r/j_i|$  and  $|j_t/j_i|$  are, respectively, equal to the 3. reflection and transmission coefficients, while the absolute value of *j* has little significance. It turns out, as shown in Figure 3, that the magnitude of the particle fluxes of both  $(|j_i| - |j_r|)$  and  $j_t$  is the same, and is fairly constant independent of x. This is a natural consequence of the stationary-state treatment of the free particle motion in one dimension.

Substituting eq 21 into eq 6, the tunnel correction factors were calculated. We are now in a position to compare the calculated values with our experimental data,<sup>7a</sup> for all the terms appearing in eq 5 have been evaluated. As shown in Figure 4, agreement between the calculated and experimental KIEs seems reasonable in view of various simplifications involved in our calculations. We have shown<sup>7</sup> that the large theoretical values of the KIE are mainly due to the much larger tunnel correction factors for the H<sup>•</sup> +  $c-C_6H_{12}$  than for the H<sup>•</sup> +  $c-C_6D_{12}$  reaction. It seems to us that tunneling plays a role in the hydrogen-atom-transfer reactions with significant activation energy.

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Registry No. D<sub>2</sub>, 7782-39-0; H<sub>2</sub>, 1333-74-0; H, 12385-13-6; c-C<sub>5</sub>H<sub>10</sub>, 287-92-3; c-C<sub>6</sub>H<sub>12</sub>, 110-82-7; c-C<sub>7</sub>H<sub>14</sub>, 291-64-5; n-C<sub>6</sub>H<sub>14</sub>, 110-54-3; *n*-C<sub>7</sub>H<sub>16</sub>, 142-82-5; *n*-C<sub>8</sub>H<sub>18</sub>, 111-65-9; CF<sub>3</sub>, 2264-21-3; CD<sub>3</sub>H, 676-80-2; O, 17778-80-2.

# One-Electron-Transfer Reactions of the Couple $SO_2/SO_2^-$ in Aqueous Solutions. Pulse **Radiolytic and Cyclic Voltammetric Studies**

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Rate constants for one-electron reduction of SO<sub>2</sub> by several radicals and for reduction of several compounds by SO<sub>2</sub><sup>--</sup> radicals were determined by pulse radiolysis at pH 1. SO<sub>2</sub> is reduced by the (CH<sub>3</sub>)<sub>2</sub>COH radicals with  $k = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and by viologen radicals and certain porphyrin  $\pi$ -radical anions with  $k \sim 10^8 - 10^9 \,\mathrm{M^{-1} \, s^{-1}}$ . The SO<sub>2</sub><sup>--</sup> radical reduces compounds which have reduction potentials more positive than -0.28 V. The rate constants for these reductions vary from  $<10^7$  to  $>10^9$  $M^{-1}$  s<sup>-1</sup> and depend on the redox potentials of the compounds and on other properties such as charge and self-exchange rate. The reduction potentials for SO<sub>2</sub> and for the porphyrins were determined by cyclic voltammetry under identical conditions. These reduction potentials were used along with the rate constants and previously reported self-exchange rates to estimate the self-exchange rate for the couple SO<sub>2</sub>/SO<sub>2</sub><sup>--</sup> in acidic solutions. The calculated values were found to vary over many orders of magnitude, similar to the situation reported before for the  $O_2/O_2^-$  couple.

#### Introduction

The radical  $SO_2^{-}$  exists in solution in equilibrium with its dimer, the dithionite ion.1

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^{*-}$$
 (1)

This equilibrium is shifted predominantly to the left;  $K_1 =$  $(0.6-1.4) \times 10^{-9}$  M was determined from ESR measurements of SO<sub>2</sub><sup>•-</sup> concentrations at equilibrium.<sup>2,3</sup> Dithionite is a reducing agent which is frequently used to reduce metalloporphyrins,<sup>4-8</sup> other metal complexes,<sup>9,10</sup> and certain organic and biological compounds.<sup>11-15</sup> It acts as a one-electron reducing agent predominantly via the SO2\*, although certain compounds were shown to be reduced directly by  $S_2O_4^{2-}$  also (but with lower rate constants, see, e.g., ref 10).

$$A + SO_2^{\bullet} \rightarrow A^{\bullet} + SO_2 \tag{2}$$

$$A + S_2 O_4^{2-} \rightarrow A^{-} + SO_2 + SO_2^{-}$$
(3)

Rates of reduction by  $S_2O_4^{2-}$  were measured by spectrophotometry or stopped-flow techniques and the rate constants for reaction 2 were derived from the overall kinetics and the equilibrium constant  $K_1$ . The values of  $k_2$  are thus dependent on the accuracy of  $K_1$  and on the condition that  $k_1$ , the rate of monomerization of dithionite, is not the rate-determining step. Furthermore, such measurements are limited to conditions under which  $S_2O_4^{2-}$  is stable, i.e. neutral and alkaline pH. To overcome

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some of these limitations we chose to study the reactions of SO<sub>2</sub><sup>--</sup> produced by one-electron reduction of SO<sub>2</sub> in a pulse radiolysis experiment.

 $SO_2$  is the stable form of S(IV) in acidic solutions.

$$SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^-, \ pK_a = 1.86^{16}$$
 (4)

It has been shown already<sup>17</sup> that SO<sub>2</sub> may be reduced by the  $CO_2^{-1}$ radical with  $k_5 = 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ 

$$\operatorname{CO}_2^{-} + \operatorname{SO}_2 \to \operatorname{CO}_2 + \operatorname{SO}_2^{-}$$
 (5)

and it is likely to be reduced by other strongly reducing radicals as well. Therefore, it should be possible to produce SO<sub>2</sub><sup>•-</sup> by pulse radiolysis of acidic solutions of SO<sub>2</sub> containing other appropriate scavengers and to follow directly the subsequent reactions of SO2\*radicals before they dimerize.

In this paper we report the rate constants for reduction of SO<sub>2</sub> by several radicals and for reduction of a number of organic compounds and metalloporphyrins by SO2. The self-exchange rate for the couple SO<sub>2</sub>/SO<sub>2</sub><sup>--</sup> was calculated from the rates of reaction with various compounds and found to be dependent on the system studied. The redox potentials for this couple and for the metalloporphyrins were determined by cyclic voltammetry.

## **Experimental Section**

The materials used were of the purest grade commercially available and were used without further purification. Sodium bisulfite was an analytical grade reagent from Mallinckrodt.<sup>18</sup> The amount of S(IV) in the bisulfite was determined by dissolving a sample in 6 M HClO<sub>4</sub> and measuring the absorbance of SO<sub>2</sub> at 280 nm,  $\epsilon = 367 \text{ M}^{-1} \text{ cm}^{-1}$  was used.<sup>19</sup> Formic acid was also Mallinckrodt AR and 2-propanol was Baker Analyzed reagent. Duroquinone (DQ) was obtained from Sigma; sodium 9,10anthraquinone-2-sulfonate (AQS) and p-nitroacetophenone (PNAP) were from Aldrich; riboflavin was from Calbiochem; and methylviologen (MV) and benzylviologen (BV) were from K&K. The porphyrins were obtained from Midcentury Chemical Co.

The metalloporphyrins used were derived from tetrakis(4sulfonatophenyl)porphyrin (TSPP), tetrakis(N-methyl-4pyridyl)porphyrin (TMPyP), tetrakis(3-pyridyl)porphyrin (TPyP), or tetrakis (N, N, N)-trimethyl-4-anilino) porphyrin (TAP). When the metal centers of the porphyrins are  $Zn^{II}$ ,  $In^{III}$ ,  $Sn^{IV}$ , or  $Sb^{V}$ , these compounds are known to undergo one-electron reduction on the ligand to form metalloporphyrin  $\pi$ -radical anions, which exhibit broad absorptions around 700 nm.<sup>20,21</sup> When the metal centers are Mn<sup>III</sup>, Fe<sup>III</sup>, or Co<sup>III</sup> the metalloporphyrins are reduced on the metal to form the divalent state.<sup>22</sup> This reduction is accompanied by smaller changes in the absorbance of the porphyrins and was followed in the 550-nm range. The reduced metalloporphyrins are more sensitive to acidic conditions and may demetallate.23 Under our experimental conditions the demetallation was always much slower than the reduction.

Acid solutions were prepared in most cases with 0.1 M HCl or HClO<sub>4</sub> and were bubbled with ultrapure nitrogen. They were examined by pulse radiolysis first in the absence of SO<sub>2</sub>; then the bubbling was replaced with a nitrogen flow above the solution and the desired amount of solid NaHSO3 was introduced into the solution. Under these conditions the bisulfite was immediately converted to  $SO_2$  which did not escape from the solution. The details of the pulse radiolysis apparatus, experimental conditions, and data processing have been described before.<sup>24</sup>

Rate constants for reduction of SO<sub>2</sub> by various radicals were determined in most cases by following the rate of decay of the reducing radical as a function of SO<sub>2</sub> concentration. The viologen radicals were monitored at 600 nm and the porphyrin radical anions at 700 nm. Reduction by the radical derived from 2propanol could not be followed in the same manner because of lack of a suitable intense absorption. Therefore, the rate of this reaction was determined by competition kinetics using AQS as the competitor.

Rate constants for reduction of the various substrates by SO2. were determined by following the buildup of absorption of the product radical as a function of substrate concentration in the presence of excess  $SO_2$ . In all cases the product formation was monitored also in the absence of  $SO_2$ , i.e. when the substrate was reduced by the  $CO_2^{\bullet-}$  or the  $(CH_3)_2COH$  radical. Reduction by  $SO_2^{\bullet-}$  was found to be always slower than by the other radicals.

Cyclic voltammetric studies were made with a Rank E611 potentiostat driven by a purpose-built triangle wave generator. A conventional three-electrode arrangement was used. The working electrode was either a freshly polished glassy carbon electrode or a gold foil. A Pt counter electrode was used in conjunction with a saturated calomel reference. All solutions contained metalloporphyrin (ca.  $5 \times 10^{-4}$  M) in water and were thoroughly deoxygenated by purging with N2. For TMPyP complexes, the aqueous solution also contained 2-propanol (20% v/v) and 0.1 M HCl. For TSPP complexes, the background electrolyte contained 0.1 M HCl + 0.1 M HCOOH. The cyclic voltammograms were recorded by plotting the current vs. applied potential at different potential scan rates (in the range of 10 mV/s to 20 V/s). The electrode surface was cleaned before each scan and the area of the electrode was determined by oxidation of ferrocyanide. The reproducibility of the peak potentials and currents was within 5% of the quoted values.

Solutions of sodium bisulfite were made by adding weighed amounts of solid material to N2 purged aqueous solutions containing 0.1 M HCl + 20% 2-propanol. The N<sub>2</sub> stream was stopped upon addition of the solid to prevent removal of SO<sub>2</sub>. In order to keep atmospheric oxygen out of the system the electrolysis cell was maintained in a small glove box under an atmosphere of N2. The concentration of NaHSO<sub>3</sub> was ca. 10<sup>-3</sup> M. For these experiments a glassy carbon working electrode was used.

### **Results and Discussion**

Reduction of  $SO_2$ . The  $SO_2^{-}$  radical in acidic solutions was produced either by reaction 5 under conditions similar to those described before<sup>17</sup> or by reaction with the 2-hydroxy-2-propyl radical

$$(CH_3)_2\dot{C}OH + SO_2 \rightarrow (CH_3)_2CO + H^+ + SO_2^{\bullet-}$$
 (6)

Pulse radiolysis of acidic solutions of 2-propanol is known to yield predominantly the  $(CH_3)_2$ COH radical. The rate constant for reaction 6 was measured by competition with the reduction of AQS, reaction 7, since direct measurement by following the absorbance of either (CH<sub>3</sub>)<sub>2</sub>COH or SO<sub>2</sub><sup>--</sup> is practically impossible.

$$(CH_3)_2\dot{C}OH + AQS \rightarrow (CH_3)_2CO + H^+ + AQS^{-}$$
 (7)

$$AQS^{\bullet-} + H^+ \Rightarrow AQSH^{\bullet} \quad (pK_a = 3.2) \quad (8)$$

By following the yield and the kinetics of formation of AQSH<sup>•</sup> at 400 nm at various [AQS] in the absence and in the presence of varying concentrations of SO<sub>2</sub> we derived  $k_7 = 3.1 \times 10^9$  and  $k_6 = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

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TABLE I: Rate Constants for Reduction of SO<sub>2</sub> and Redox Potentials of the Reducing Radicals

reducing radical	$k, M^{-1} s^{-1}$	$E^1$ , V vs. NHE
(CH <sub>3</sub> ) <sub>2</sub> ĊOH	$2.1 \times 10^{9}$	-1.2ª
MV.+	$1.2 \times 10^{9}$	$-0.45^{b}$
BV**	$5 \times 10^{8}$	-0.38 <sup>b</sup>
ZnTMPyP*3+	$8 \times 10^{8}$	-0.69°
InTMPyP*4+	$2 \times 10^{8}$	-0.51 <sup>c</sup>

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Figure 1. Effect of pH on the rate of reduction of  $SO_2/HSO_3^-$  (6 × 10<sup>-5</sup> M) by MV\*+.

It should be pointed out that the SO<sub>2</sub><sup>--</sup> formed by reaction 6 in competition with reaction 7 subsequently reduces AQS

$$SO_2^{-} + AQS \rightarrow SO_2 + AQS^{-}$$
 (9)

but the rate constant for this reaction is about 25 times lower than  $k_7$  (see below) so that the two processes were completely resolved.

The rate constants for reduction of  $SO_2$  by the viologen radicals and two metalloporphyrin  $\pi$ -radical anions were measured by following the decay of these radicals as a function of [SO<sub>2</sub>]. The results are presented in Table I. Reduction of SO<sub>2</sub> by the methylviologen radical takes place with a nearly diffusion-controlled rate constant,  $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ 

$$MV^{+} + SO_2 \rightarrow MV^{2+} + SO_2^{-}$$
(10)

The rate constant for the benzylviologen is slightly lower, in accordance with the lower driving force of its reaction with SO<sub>2</sub>. The rate constant for the reaction of MV\*+ was found to be strongly pH dependent (Figure 1) due to the acid-base equilibrium 4, i.e.  $MV^{*+}$  reduces  $SO_2$  but does not reduce  $HSO_3^{--}$ .

$$MV^{*+} + HSO_3^- + H^+ \rightleftharpoons MV^{2+} + SO_2^{*-} + H_2O$$
 (11)

Equilibrium 11 lies predominantly to the left due to the higher redox potential of HSO<sub>3</sub><sup>-</sup> as compared with SO<sub>2</sub>. Experimentally, however, it was found<sup>25</sup> to be drawn to the right as a result of the dimerization of SO<sub>2</sub><sup>•-</sup> to S<sub>2</sub>O<sub>4</sub><sup>2-</sup>. From  $k_{10}$  for MV<sup>++</sup> and BV<sup>++</sup> and from the redox potentials

of these radicals (Table I) and the redox potential of SO<sub>2</sub>/SO<sub>2</sub>. we calculate the rate constants for the reverse reactions, i.e. for reduction of the viologens by  $SO_2^{\bullet-}$ , of  $1.2 \times 10^6$  and  $1.4 \times 10^7$  $M^{-1}$  s<sup>-1</sup>, respectively. The corresponding values measured by the dithionite stopped-flow experiments in neutral solutions are somewhat higher,  $9 \times 10^6$  and  $9 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup>, respectively.<sup>13</sup>

The two metalloporphyrin  $\pi$ -radical anions, formed by reduction of Zn- and InTMPyP, reduce SO<sub>2</sub> with rate constants that increase with the driving force, as is the case with the viologen radicals. But the absolute values for the porphyrins are not higher than

TABLE II: Rate Constants for Reduction of Various Compounds by SO2<sup>--</sup> and Electrochemical Results on These Compounds

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	<i>k</i> ,	$E^{1,a}$	$D,^b$	k <sub>o</sub> ,c
compound	M <sup>-1</sup> s <sup>-1</sup>	V vs. NHE	$10^{-6} \text{ cm}^2 \text{ s}^{-1}$	$10^{-3} \text{ cm s}^{-1}$
PNAP	$2.6 \times 10^{7}$	-0.252 <sup>d</sup>		· · · · · · · · · · · · · · · · · · ·
AQS	$1.3 \times 10^{8}$	$-0.240^{d}$		
riboflavin	$4.0 \times 10^{8}$	-0.138 <sup>e</sup>		
DQ	$1.4 \times 10^{9}$	$0.004^{d}$		
IrCl <sub>6</sub> <sup>2-</sup>	$1.1 \times 10^{9}$	0.89		
Mn <sup>III</sup> TSPP <sup>3-</sup>	<b>≤</b> 10 <sup>7</sup>	-0.19	2.48	
Mn <sup>III</sup> TMPyP <sup>5+</sup>	$4.6 \times 10^{8}$	0.02	1.79	1.04
Fe <sup>III</sup> TSPP <sup>3-</sup>	$1.2 \times 10^{8}$	-0.11	2.61	
Fe <sup>III</sup> TMPyP <sup>5+</sup>	$3.4 \times 10^{9}$	0.162	1.35	2.06
Co <sup>III</sup> TSPP <sup>3-</sup>	$4 \times 10^{7}$	0.202	1.88	1.08
Co <sup>III</sup> TMPyP <sup>5+</sup>	$2 \times 10^{8}$	0.422	2.12	1.27
Co <sup>III</sup> TAP <sup>5+</sup>	$1.9 \times 10^{8}$	0.21	2.2	
Sn <sup>IV</sup> TMPyP <sup>6+</sup>	$1.6 \times 10^{9}$	-0.138	3.62	4.62
Sb <sup>v</sup> TPyP <sup>7+</sup>	$2.7 \times 10^{9}$	-0.020	4.32	5.28

<sup>a</sup>One-electron reduction potentials reported previously or half-wave potentials determined for the porphyrins in this work by cyclic voltammetry. <sup>b</sup> Diffusion coefficient. <sup>c</sup> Electrochemical rate constants. <sup>d</sup> Reference 26. <sup>e</sup> Reference 27. <sup>f</sup> Margerum, D. W.; Chellappa, K. L.; Bossu, F. P.; Burce, G. L. J. Am. Chem. Soc. 1975, 97, 6894.

those for the viologens as may be expected from the redox potentials (Table I). This discrepancy probably results from differences in the self-exchange rates of the viologens vs. the porphyrins (see below).

Reduction of  $SO_2$  by the radical anion of ZnTMPyP was monitored by following the decay of the porphyrin radical at 700 nm on a time scale of 0.1-0.2 ms. In these experiments it was noticed that at longer times, 1-2 ms, the absorption increases. The spectrum at long times was different than that of the initial anion radical. Its maximum was at 660 nm and its width at half-height was about 100 nm. This spectrum is ascribed to a species formed by the reaction of SO<sub>2</sub><sup>••</sup> with ZnTMPyP which is not an electron-transfer reaction to the porphyrin  $\pi$ -system. It is known that excess dithionite destroys the TMPyP ligand in many metalloporphyrins (see, e.g., ref 4), and the reaction observed here may be the initial step leading to that destruction. The rate constant for the reaction is approximately  $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and its mechanism may involve addition of the radical to the porphyrin.

Reduction by  $SO_2^{\bullet-}$ . The rate constants for reduction of various compounds by  $SO_2^{\bullet-}$  radicals in acid solutions are summarized in Table II. For the organic compounds *p*-nitroacetophenone, anthraquinone-2-sulfonate, riboflavin, and duroquinone the rate constants for reduction by  $SO_2^{-}$  increase from 2.6 × 10<sup>7</sup> to 1.4  $\times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. This increase follows the rise in reduction potential<sup>26,27</sup> as expected from the Marcus relation.<sup>28</sup> Rate constants which are considerably lower than 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup> cannot be easily determined due to the rapid dimerization of SO2<sup>--</sup>. Rate constants above  $\sim 3 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> approach the diffusion-controlled limit and are not expected to exhibit the increase in k with increase in  $E^1$ . Moreover, compounds with more positive  $E^1$  often cannot be experimentally measured due to their thermal reaction with bisulfite or SO<sub>2</sub> prior to the pulse, as was found with benzoquinone.

The rate constants for reduction of the various metalloporphyrins by SO<sub>2</sub><sup>•-</sup> vary from  $<10^7$  to  $3.4 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. Their dependence on redox potential is obvious only for porphyrins with the same metal center since such porphyrins usually have the same self-exchange rates.<sup>29</sup> When the metal center is different, however, the self-exchange rate may be also different, often by several orders of magnitude, and this, of course, affects the rate of reduction. Furthermore, the overall charge of the porphyrins varies from 7+ to 3- so that the electrostatic effect on the rate of reaction with  $SO_2^{\bullet-}$  is considerable. More quantitative treatment of these results is attempted by using the Marcus cross relation equation and the self-exchange rates (see below).

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Figure 2. Typical cyclic voltammograms recorded in 0.1 M HCl solutions containing 20% v/v 2-propanol: (a) CoTMPyP, (b) FeTMPyP, (c) SbTPyP, (d) SnTMPyP, (e) NaHSO3. Experimental conditions as given in the text.

The rate constants for reduction of the porphyrins are only partially in agreement with those determined previously by the dithionite method in neutral solutions. Our value for FeTSPP is in the same range as the rate constants determined for several other Fe<sup>III</sup>-porphyrins,<sup>6</sup> and our values for MnTSPP and CoTMPyP are similar to those reported before using dithionite.<sup>8</sup> On the other hand, the rate constants we measured for MnTMPyP and FeTMPvP are, respectively, one and two orders of magnitude higher than those determined by the dithionite method.<sup>8</sup> A difference of this magnitude is not likely to result from the pH change between the two experiments since the axial ligation on these porphyrins and their redox potentials do not change between pH 7 and pH 1. (The presence of excess  $SO_2$  also was found to have no effect on the redox potentials determined by cyclic voltammetry, see below.) Our rate constants for CoTSPP and CoTAP also are much higher than values reported for other Co<sup>III</sup>-porphyrins.<sup>5</sup> The reason for this discrepancy is unclear.

Rate constants for reduction of several compounds by SO2. were found to be generally  $\sim 1000$  times greater than those for reduction by  $O_2^{-,30}$  That ratio does not hold for the porphyrins. Using the reported<sup>31</sup> rate constants for  $O_2^-$  we find a ratio of ~15 for FeTMPyP, CoTMPyP, and FeTSPP, and a ratio of 9 for MnTMPyP. These lower ratios must be the result of the overall high rate constants for these porphyrins as compared with those of the compounds considered before. For duroquinone, the rate constant reported for  $O_2^-$  is  $4.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , <sup>32</sup> which is 310 times smaller than that for SO<sub>2</sub><sup>-</sup>, in line with the previous ratios. On the other hand, for PNAP the reaction with O<sub>2</sub><sup>-</sup> is less favorable; we calculate a rate constant of  $5.7 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  (from the reverse rate constant of  $1.4 \times 10^{633}$  and the redox potentials of -0.355and -0.155 for PNAP and O2, respectively). This rate constant is  $4.5 \times 10^4$  times slower than that for  $SO_2^{**}$  + PNAP. It is reasonable to expect that the ratio of  $k(SO_2^{\bullet})/k(O_2^{-})$  will increase as the absolute rate constants decrease, as is found here.

Cyclic Voltammetric Measurements. The redox potentials for some of the compounds examined in this study have been measured before and are given in Tables I and II. For the porphyrins, redox potentials were measured mainly in neutral solutions and, although in several cases these are not expected to change between pH 7 and pH 1, we determined the redox potentials for all the porphyrins at pH 1.

Cyclic voltammograms were recorded for each of the compounds in N<sub>2</sub>-saturated solution. Several examples are shown in Figure 2. For Co<sup>III</sup>TMPyP, Co<sup>III</sup>TSPP, Co<sup>III</sup>TÂP, Fe<sup>III</sup>TMPyP, Sb<sup>v</sup>TPyP, and Sn<sup>Iv</sup>TMPyP the voltammograms showed quasireversible electrochemical behavior, i.e. the peak currents observed upon the forward (cathodic) scan were of equal magnitude to those observed upon the reverse (anodic) scan. The magnitude of the forward peak current  $(i_p)$  could be interpreted in terms of the following equation<sup>34</sup>

$$i_{\rm p} = 2.69 \times 10^5 A C_0 D^{1/2} v^{1/2}$$
 (12)

where A is the electrode area,  $C_0$  is the initial concentration of electrode-active material, D is the diffusion coefficient of the species, and v is the potential scan rate (V/s). All the above compounds gave linear plots of  $i_p$  vs.  $v^{1/2}$  from which values of D were estimated. The separation between anodic and cathodic peaks also depended upon potential scan rate and approached 60 mV at very slow scan rates.

For these compounds, the half-wave potentials for one-electron reduction  $(E_{1/2})$  were determined as the average of the cathodic and anodic peak potentials at slow scan rates. The potential range was restricted to about 150-200 mV beyond the cathodic peak to avoid problems of further reduction.

In contrast with the above cases, Mn<sup>III</sup>TMPyP, Mn<sup>III</sup>TSPP, and Fe<sup>III</sup>TSPP showed nonreversible electrochemical behavior upon one-electron reduction. A clear peak was seen upon the cathodic scan for which the peak current and potential depend upon the scan rate, showing that the electrode process is diffusion controlled. However, no peak could be resolved upon the anodic scan. For these compounds it appears that demetallation follows the reduction step so that the divalent metalloporphyrin is too unstable to be detected on the reverse scan. Indeed, for MnTMPyP the free base porphyrin adsorbs onto the electrode surface and can be detected upon multiple scanning.

For these metalloporphyrins, plots of  $i_p$  vs.  $v^{1/2}$  were linear and allowed determination of diffusion coefficients. Linear plots were also obtained for peak potential  $(E_p)$  vs. log v, from which half-wave potentials were derived according to<sup>35</sup>

$$E_{\rm p} = E_{1/2} - 0.78(RT/nF) - (RT/nF) \ln (kRT/nFv)$$
(13)

where k is the pseudo-first-order rate constant for demetallation.

Where information exists, the measured half-wave potentials (Table II) are in very good agreement with literature values. For example,  $E_{1/2}$  values have been reported for CoTMPyP in 0.01 M HNO<sub>3</sub> (0.415 V),<sup>36</sup> FeTMPyP in 0.1 M HCl (0.16 V),<sup>37</sup> MnTMPyP in water of pH 5.2 (-0.02 V),<sup>38</sup> SnTMPyP at pH 5 (-0.28 V),<sup>20</sup> and SbTPyP at pH 5 (-0.20 V).<sup>20</sup> For Co, Fe, and Mn porphyrins the electron is added to the central metal ion causing reduction of the trivalent ion, while for Sn and Sb porphyrins the electron is added to the porphyrin ring. Within the limited data, the difference in redox potential between TMPyP and TSPP complexes with a given metal ion is ca.  $230 \pm 40$  mV. The fact that the TMPyP complexes are the easier to reduce is to be expected on the basis of their electron-donating properties. The relative ease of demetallation is also consistent with known trends.23,29

The derived diffusion coefficients (Table II) are in line with expected values with respect of the molecular size of the compounds. Where the electrochemistry followed quasireversible behavior, electrochemical rate constants were determined from the peak separation as a function of scan rate.<sup>34</sup> The derived rate constants  $(k_0)$  (Table II) show that it is easier to add an electron to the porphyrin ring than to the central metal ion. Presumably,

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**TABLE III: Calculation of Self-Exchange Rate Constants** 

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reaction	$k_{12}{}^{a}$	K <sub>12</sub> <sup>b</sup>	k <sub>11</sub> <sup>c</sup>	$k(SO_2/SO_2^{\bullet-})$	$f_{12}$
$MV^{+} + SO_2$	$1.5 \times 10^{9}$	$5.6 \times 10^{2}$	$1 \times 10^{6 d}$	$8.2 \times 10^{9}$	0.49
SO <sub>2</sub> •- + MnTMPyP	$4.9 \times 10^{8}$	$1.7 \times 10^{5}$	$3 \times 10^{3 e}$	$2.7 \times 10^{9}$	0.18
SO <sub>2</sub> <sup>•-</sup> + FeTMPyP	$7.8 \times 10^{9}$	$4.2 \times 10^{7}$	$1 \times 10^{6f}$	$9.3 \times 10^{7}$	0.02
$SO_2^{\bullet-}$ + FeTSPP	$1.9 \times 10^{8}$	$1.0 \times 10^{3}$	$1 \times 10^{6f}$	$6.8 \times 10^{7}$	0.53
$SO_2^{-} + CoTMPyP$	$2 \times 10^{8}$	$1.1 \times 10^{12}$	20 <sup>g</sup>	$4.7 \times 10^{5}$	$4 \times 10^{-3}$
$SO_2^{-} + CoTSPP$	$4 \times 10^{7}$	$2.0 \times 10^{8}$	20 <sup>g</sup>	$7.0 \times 10^{6}$	0.057
$SO_2^{-} + CoTAP$	$1.9 \times 10^{8}$	$2.8 \times 10^{8}$	20 <sup>g</sup>	$1.7 \times 10^{8}$	0.037
$SO_2^{} + IrCl_6^{2}$	$1.4 \times 10^{9}$	$9 \times 10^{19}$	$2.3 \times 10^{5 h}$	$2.8 \times 10^{-2}$	$3 \times 10^{-6}$

<sup>a</sup>Rate constants for the reaction listed, in M<sup>-1</sup> s<sup>-1</sup>, determined in this work and corrected for the effect of the diffusion-controlled limit by the equation  $k_{act}^{-1} = k_{obsd}^{-1} - k_{diff}^{-1}$  taking  $k_{diff} = 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . <sup>b</sup> Equilibrium constants determined from known redox potentials listed in Tables I and II and taking  $E_{1/2} = -0.288$  V for the SO<sub>2</sub>/SO<sub>2</sub><sup>--</sup> couple. Self-exchange rate constants for the couple reacting with SO<sub>2</sub>/SO<sub>2</sub><sup>--</sup>, in M<sup>-1</sup> s<sup>-1</sup>. <sup>d</sup> From ref 44. <sup>e</sup> From ref 29, taken to be similar to the values for the other Mn-porphyrins determined. <sup>f</sup>Average from ref 6 and ref 45. <sup>g</sup>From ref 36 and 46. <sup>h</sup> From Pennington, D. E. In Coordination Chemistry, Martell, A. E., Ed.; American Chemical Society: Washington, DC, 1978; Monograph 174, Vol. 2, Chapter 3.

this is connected with geometric factors since the metal ion is screened by axial ligands and by the porphyrin ring. Also,  $k_0$  is influenced by the self-exchange rate of the couple and, in most cases, this is much slower for reduction of a metal ions than for reduction of a large organic moiety.

The cyclic voltammograms recorded with aqueous solutions of NaHSO<sub>3</sub> at pH 1 were highly irreversible (Figure 2e). Sharp peaks (half-widths ca. 40 mV) were found upon the cathodic scans but no peaks could be resolved upon the reverse anodic scans. Again, the peak current and potential depended upon scan rate showing that the electrode process was diffusion controlled. For this system the most probable reaction scheme is

$$SO_2 + e \rightarrow SO_2^{-}$$
 (14)

$$2SO_2^{\bullet-} \rightarrow S_2O_4^{2-} \tag{15}$$

for which the peak potential is related to the half-wave potential by<sup>39</sup>

$$E_{\rm p} = E_{1/2} - 0.9(RT/nF) + (RT/3nF) \ln (2kC_0RT/3nFv)$$
(16)

In principle, the bimolecular rate constant for dimerization of the  $SO_2^{-}$  radical (k) can be estimated by this technique but it is too fast for accurate determination. From the above relationship, the half-wave potential for the SO<sub>2</sub>/SO<sub>2</sub><sup>--</sup> couple at pH 1 was found to be -0.288 V vs. NHE. This value is in very good agreement with that calculated before,<sup>40</sup> and it indicates that  $SO_2^{*-}$  is able to reduce all the metalloporphyrins listed in Table II, although there is a large spread in thermodynamic driving force for electron transfer.

At pH 1 it was found that the peak potential was independent of ionic strength (<2 M) and only slightly dependent upon concentration of NaHSO3. It does depend, however, upon pH. For HCl concentrations of 0.01, 0.1, 0.5, 1.0, and 2.0 M  $E_p$  values of -0.31, -0.29, -0.23, -0.17, and -0.13 V were found, respectively (Figure 3). This pH effect suggests that the radical is protonated in strongly acidic solutions.

$$SO_2^{\bullet-} + H^+ \rightleftharpoons SO_2 H^{\bullet}$$
 (17)

Unfortunately, the pH dependence cannot be studied at lower pH because of  $H_2$  liberation at the electrode surface and thus the pK for the above transition cannot be determined by this technique.

Self-Exchange Rate Constants. The self-exchange rate constant for the couple  $SO_2/SO_2^{\bullet-}$  was estimated to be  $3.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1.40}$ This value was based on recalculation of earlier results on the redox potential of SO<sub>2</sub><sup>--</sup> and its self-exchange rate, taking into account the pH effect in going from  $HSO_3^{-}/SO_2^{-}$  to the  $SO_2/SO_2^{-}$  couple. Our results provide a direct measurement of the redox potential of the  $SO_2/SO_2^{-}$  couple, which is very close to the calculated value. Since the self-exchange rates for several of the reactants listed in Tables I and II have been reported in previous studies, we can calculate the self-exchange rate for  $SO_2/SO_2^-$  from these rate



Figure 3. Effect of pH on the reduction potential of  $SO_2$ .

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constants. The calculations were made by using the Marcus cross-relation equations

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12}$$
(18)

$$n f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RI]^2}{4[\ln (k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT]}$$
(19)

$$W_{12} = \exp\left[\frac{-(w_{12} + w_{21} - w_{11} - w_{22})}{2RT}\right]$$
(20)

$$w_{ab} = \frac{4.23 \times 10^{-8} Z_a Z_b}{r(1 + 3.28 \times 10^7 r(\mu^{1/2}))}$$
(21)

as outlined before.<sup>40–43</sup> The results summarized in Table III were obtained by using eq 18 and 19 without taking into account the work terms.

By using the self-exchange rates reported for  $MV^{44}$  and for MnTMPyP (Table III) we calculate  $k(SO_2/SO_2^{-})$  of the order of 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>. With Fe-porphyrins, if we assume the same self-exchange rate $^{6,45}$  for both of them, as suggested before,<sup>29</sup> we obtain  $k(SO_2/SO_2^{\bullet-}) = (7-9) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . With the Coporphyrins, taking  $k_{11} = 20 \text{ M}^{-1} \text{ s}^{-1}$  for all three compounds,<sup>36,46</sup> we calculate  $k(SO_2/SO_2^{-})$  between  $5 \times 10^5$  and  $\sim 2 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>. Thus  $k(SO_2/SO_2^{\bullet-})$  varies over four orders of magnitude. More complete calculations which take into account the work terms according to eq 18-21 gave as much variations in k- $(SO_2/SO_2^{\bullet-})$  as before. The corrections for the work terms change the calculated self-exchange rates by 1-3 orders of magnitude, but the result is very much dependent on the radius assumed for the reacting species and, of course, on their charge. With the porphyrins, it has been suggested that the four positive or negative

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charges on the porphyrin periphery do not exert the same effect as a point charge or a uniformly distributed charge (see, e.g., ref 22a). Moreover, the reference self-exchange rates listed in Table III were calculated in most cases by disregarding the work terms. Because of all these reasons it was decided to present only the results obtained without accounting for work terms (Table III).

From the rate of reduction of  $IrCl_6^{2-}$  we calculate a very low value of  $k(SO_2/SO_2^{-})$ , in disagreement with the other values. The reason for the difference may lie in the fact that  $K_{12}$  in this case is very high, so that the rate of electron transfer  $k_{12}$  may be low due to the effect predicted by the "inverted region" of the Marcus relationship, i.e. when further increase in driving force results in slowing down the reaction.

A previous estimate of the self-exchange rate of  $SO_2/SO_2^{-}$  of  $3 \times 10^2$  M<sup>-1</sup> s<sup>-1</sup> was derived<sup>40</sup> from rate constants with two cobalt complexes.9 On the other hand, from reactions with viologens13 there was an indication of a very high self-exchange rate for  $SO_2/SO_2^{\bullet-}$  as is found here with methylviologen and the porphyrins. Taking all these results into account, we found k- $(SO_2/SO_2^{\bullet-})$  to vary over many orders of magnitude. The variations in  $k(SO_2/SO_2^{\bullet-})$  are reminescent of the wide variations found in the self-exchange rates for  $O_2/O_2^{\bullet-.47}$  This is not surprising since the behavior of SO<sub>2</sub><sup>•-</sup> was suggested to parallel that of  $\tilde{O_2^{-,30}}$  Such variations may be a general characteristic of redox pairs composed of a small number of atoms and one form of which is neutral, so that solvation of the two species varies greatly.<sup>47</sup> Similar but smaller variations were noticed also in the reactions of ClO<sub>2</sub> with different types of compounds.<sup>48</sup>

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**Registry No.** SO<sub>2</sub>, 7446-09-5; (CH<sub>3</sub>)<sub>2</sub>COH, 5131-95-3; MV<sup>++</sup>, 25239-55-8; BV<sup>++</sup>, 49765-27-7; ZnTMPyP<sup>+3+</sup>, 79346-68-2; InTMPyP<sup>+4+</sup>, 106589-46-2; PNAP, 100-19-6; HSO<sub>3</sub><sup>-</sup>, 15181-46-1; DQ, 527-17-3;  $IrCl_6^{2-}$ , 16918-91-5;  $Mn^{III}TSPP^{3-}$ , 88992-32-9;  $Mn^{III}TMPyP^{5+}$ , 70649-54-6; Fe<sup>III</sup>TSPP<sup>3-</sup>, 60489-11-4; Fe<sup>III</sup>TMPyP<sup>5+</sup>, 60489-13-6; Co<sup>III</sup>TSPP<sup>3-</sup>, 91629-46-8; Co<sup>III</sup>TMPyP<sup>5+</sup>, 51329-41-0; Co<sup>III</sup>TAP<sup>5+</sup>, 79619-73-1; Sn<sup>IV</sup>TMPyP<sup>6+</sup>, 89087-88-7; Sb<sup>V</sup>TPyP<sup>7+</sup>, 106904-62-5; riboflavin, 83-88-5; SO2\*, 12143-17-8; AQS, 131-08-8.

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# A Time-Resolved Study of Singlet Molecular Oxygen ( $^{1}\Delta_{a}O_{2}$ ) Formation in a Solution-Phase Photosensitized Reaction: A New Experimental Technique To Examine the Dynamics of Quenching by Oxygen

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The solution-phase, time-resolved phosphorescence of singlet molecular oxygen  $({}^{1}\Delta_{g}O_{2})$ , created by energy transfer from a sensitizer, has been examined by using a near-infrared detection system capable of resolving events that result in the formation of  $\Delta_2 O_2$ . As a method by which to examine oxygen quenching reactions, this approach is seen to complement flash absorption studies. Unlike existing experimental techniques, however, our approach is uniquely sensitive to rate-limiting steps that might exist during the energy-transfer process to form  ${}^{1}\Delta_{g}O_{2}$ . In this report, we present oxygen quenching rate constants for the triplet state of five different molecules in several solvents. In addition, we suggest that a static quenching component may be involved in the oxygen-induced deactivation of a triplet state.

#### Introduction

The deactivation of excited-state organic and biological molecules by molecular oxygen has long been a subject of scientific study.<sup>1-5</sup> Attempts to characterize the organic molecule-oxygen interaction have included: (a) the chemical trapping of photooxygenated molecules,<sup>2,6,7</sup> (b) both time-resolved and steady-state fluorescence studies,<sup>1,8</sup> and (c) flash absorption studies of molecular triplet states.<sup>3,5,7,9</sup> Although results of these studies have contributed a great deal to our understanding of the mechanism by which molecular oxygen quenches an excited state, a complete and accurate description of this interaction is still lacking. This

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is particularly true of the reaction channel which results in energy transfer to form singlet molecular oxygen  $({}^{1}\Delta_{g}O_{2}).^{6,7}$ 

It has recently become feasible to detect the near-infrared phosphorescence of  ${}^{1}\Delta_{g}O_{2}$  ( ${}^{3}\Sigma_{g}^{-}O_{2} \leftarrow {}^{1}\Delta_{g}O_{2}$ ; 1270 nm, 7874 cm<sup>-1</sup>) in a solution-phase time-resolved experiment.<sup>10-14</sup> This technique has subsequently become indispensable in studies of  ${}^{1}\Delta_{e}O_{2}$  decay dynamics.<sup>15-17</sup> In addition, examination of the intensity of this luminescence has provided insight into the efficiency of  ${}^{1}\Delta_{g}O_{2}$ formation in a photosensitized process.<sup>18-23</sup> Unfortunately,

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