In Situ Spectroelectrochemical Studies of Oxygen Reduction in Dimethyl Sulfoxide and Pyridine

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Electrochemical reduction of oxygen has been studied employing in situ spectroelectrochemical techniques, and the results are reported. Absorption spectra of the electrogenerated superoxide ion recorded during the reduction of oxygen show maximum absorbances at 271 and 305 nm in dimethyl sulfoxide and pyridine, respectively. Molar absorptivities of 2006 (±74) and 768 (±58) $L \cdot mol^{-1} \cdot cm^{-1}$ have been determined for electrogenerated superoxide ions in DMSO and pyridine by employing cyclic voltammetric peak currents and respective derivative cyclic voltabsorptometric signals. The significant red shift observed for the absorption band in pyridine is explained by the difference in solvation energies of the superoxide ion in two solvents. The electrokinetic parameters obtained in these solvents are also consistent with this model.

Introduction

It has been well established in the literature[1-4] that superoxide ions are generated by a one-electron reduction of oxygen in nonaqueous solutions. The electrogenerated superoxide ion has been shown to be stable in nonaqueous solvents, particularly in dimethyl sulfoxide (DMSO), pyridine, dimethyl formamide, etc. Superoxide ions can also be produced from hydrogen peroxide by its reduction[5] or reaction with hydroxide[6] in nonprotic solvents.

Despite its demonstrated stability, the absorption spectrum of the electrogenerated superoxide ion recorded in situ has not been reported. This is perhaps because the absorption band is located in an inconvenient spectral region for spectroelectrochemical measurements, and also its molar absorptivitiy is relatively low to be recorded easily with the techniques. In most spectroelectrochemical experiments,[7] an optically transparent electrode (OTE) is used, and materials used to fabricate OTEs, including antimony-doped tin oxide films, are strongly absorbing in the region where the superoxide absorbs. We have recently constructed a near-normal incidence reflectance spectroelectrochemical (NNIRS) setup using a bifurcated quartz optical fiber,[8] which avoids the problem that the OTE has in the UV region.

Slough[9] was the first one to attempt at recording the spectrum of electrogenerated superoxide ions in pyridine in the UV–visible region, but unfortunately, the spectrum was taken in a spectral region above 340 nm, where the superoxide ion does not absorb. He reported an absorption maximum (λ_{max}) of 443 nm (2.80 eV) without presenting an actual spectrum, which was interpreted as a charge transfer band between the superoxide ion and the solvent, pyridine. Czapski and Dorfman[10,11] reported the spectrum of the superoxide ion generated in aqueous solution of pH 7.2 during pulse radiolysis of the oxygen-saturated formate solution, which showed an absorption maximum at 240 nm with a molar absorptivity (ϵ_{max}) of 1070 ± 150 $L \cdot mol^{-1} \cdot cm^{-1}$. Matheson and Lee[12] reported the spectrum with a λ_{max} of 246 ± 5 nm and ϵ_{max} of 1200 ± 100 $L \cdot mol^{-1} \cdot cm^{-1}$ in a DMSO solution prepared from commercially available potassium superoxide. Most recently, Sawyer et al. reported a λ_{max} of 253 nm with an ϵ_{max} of 10 100 $L \cdot mol^{-1} \cdot cm^{-1}$ for tetramethylammonium superoxide.[13,14]

In our current communication, we describe absorption spectra of the electrogenerated superoxide ion in DMSO and pyridine. Also, molar absorptivities have been determined by comparing the cyclic voltammetric (CV) peak current with corresponding derivative cyclic voltabsorptometric (DCVA) signals.[15,16] Electrode kinetic parameters have also been determined employing chronocoulometric and chronoabsorptometric measurements.

Experimental Section

MCB's OmniSolve DMSO and Fischer's ACS certified pyridine were used after they were dried over activated molecular sieves for a few days and purified by fractional distillation. Southwestern Analytical's electrometric grade tetra-*n*-butylammonium perchlorate (TBAP) was used as a supporting electrolyte after being dried overnight on a vacuum line. Locally acquired oxygen was used after passing it through a Matheson gas purifier. Spectra were recorded by stepping a potential to a given value, determined from cyclic voltammograms (CVs) recorded prior to the spectroelectrochemical experiments, on a reflective platinum working electrode (geometric area = 0.331 cm^2) in an oxygen-saturated DMSO or pyridine solution containing 0.10 M TBAP, employing NNIRS techniques described elsewhere.[8] The working electrode was polished to a mirror finish with Fischer 0.2-μm alumina powder before spectroelectrochemical measurements. A platinum-wire spiral was used as a counter electrode, and a silver wire was used as a pseudoreference electrode to keep the solution from being contaminated by water. A single or two compartment cell was used for the experiments.

A Princeton Applied Research (PAR) 173 potentiostat–galvanostat along with a PAR 175 universal programmer was used for recording CVs and controlling potentials. Instruments used in these experiments were interfaced to a Zenith-158 computer; instrument control and data acquisition were accomplished by the computer.

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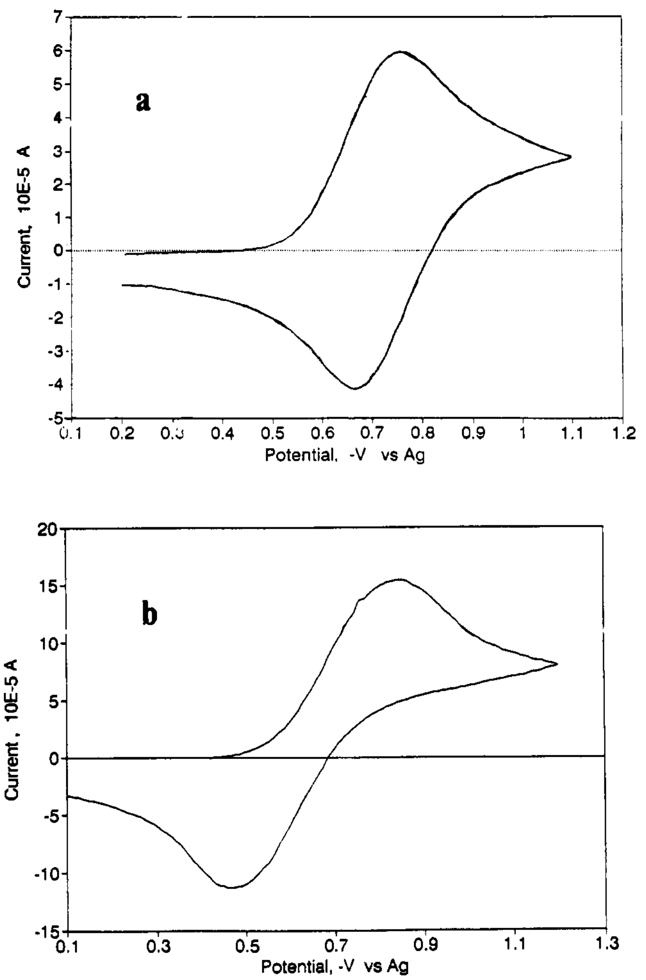

Figure 1. Cyclic voltammograms for the reduction of oxygen saturated in DMSO (a) and pyridine (b) solutions containing 0.10 M TBAP as a supporting electrolyte. Scan rate was 50 mV/s.

Results

Spectra of Electrogenerated Superoxide Ions. Figure 1 shows typical cyclic voltammograms recorded for the oxygen reduction in oxygen-saturated DMSO (a) and pyridine (b) solutions. The CV behaviors are in excellent agreement with those reported in the literature.[1-4,17] The electrochemical reduction of oxygen in DMSO is chemically reversible as the electrogenerated superoxide ion is shown to be stable in these solutions, but the reaction may be described as electrochemically "quasi-reversible", particularly in pyridine. Sawyer et al.[17] reported that the electrode material as well as solvent affects the electrochemical reversibility of the oxygen reduction. Note also in CVs that the peak current in pyridine is more than twice of that in DMSO. This is because the solubility of oxygen is much greater in pyridine than in DMSO. Concentrations of the saturated solution are 2.1 and 4.9 mM in oxygen in DMSO and pyridine, respectively, at atmospheric pressure.[17]

Figure 2 shows two spectra of the electrogenerated superoxide ion in a DMSO solution, one recorded at an applied potential of –0.8 V vs a Ag-wire pseudoreference electrode (a) and the second at –0.9 V (b). The spectral feature remains identical at two different applied potentials; the only difference is their absorbance values due to the difference in superoxide ion concentrations owing to different rates of the electron transfer reaction at different potentials. This was true for all potentials applied, indicating that only one species, i.e., superoxide ion, is being generated. The spectral shape is in general agreement with those reported earlier,[10-13] but the absorption maximum appears in the region 269–272 nm with the most frequently observed peak at 271 nm, which is red-shifted compared to those reported earlier by about 25–30 nm. Also, the absorbance is shown to be directly proportional to the partial pressure of oxygen when they are recorded at a diffusion-controlled region.

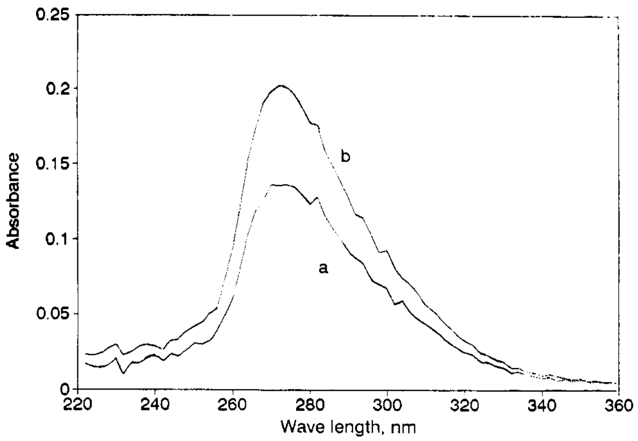

Figure 2. Absorption spectra obtained during the electrolysis at applied potentials of (a) –0.80 V and (b) –0.90 V vs. the Ag wire pseudo reference electrode in a DMSO solution saturated with oxygen.

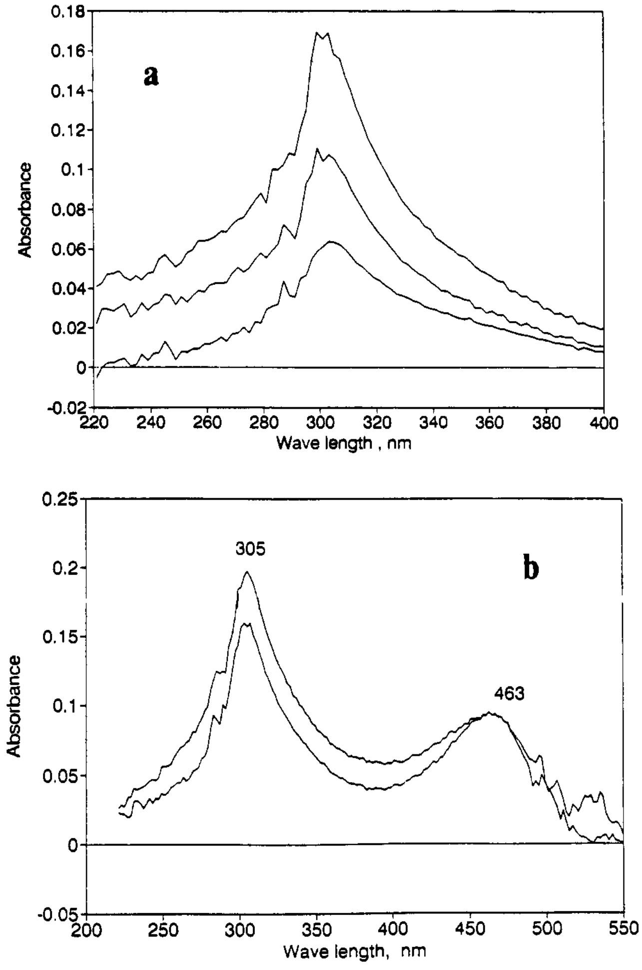

Figure 3. Absorption spectra obtained during the electrolysis at an applied potential of –0.90 V in an oxygen-saturated pyridine solution under "well-controlled" (a) and "poorly controlled" (b) conditions. Spectra in part a were recorded at –0.70, –0.80, and –0.90 V and in part b at –0.70 and –0.80 V, respectively, in ascending order. See text for details of electrolysis conditions.

Shown in Figure 3a are the spectra recorded from electrogenerated superoxide ion in pyridine under "well-controlled" conditions (vide infra). The maximum absorption occurs at a

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(17) Sawyer, D. T.; Cheiricato, G., Jr.; Angells, C. T.; Nanni, E. J., Jr.; Tsuchiya, T. *Anal. Chem.* **1982**, *54*, 1720.

significantly longer wavelength, 305 nm, than that in DMSO. Also, there appears to be a shoulder absorption at about 280 nm; we were not convinced even after several repeated experiments whether this was an experimental artifact or a spectral feature. This could be due to trace amounts of impurities such as Py(•OH), generated during electrolysis.[13,17] Also, the absorbance obtained in pyridine is somewhat lower than that in DMSO, even though the oxygen concentration is higher in pyridine. From this observation, one may deduce that the molar absorptivity must be significantly smaller in pyridine than in DMSO.

When the experiment is conducted in a single compartment cell under the conditions where the counter electrode can be excessively polarized, the spectra shown in Figure 3b are obtained. Here another absorption peak at 463 nm is observed. From an extensive number of experiments, we found that the extra absorption peak at longer wavelength is not observed when the oxygen reduction is carried out in (1) a well-purified pyridine, (2) a two-compartment cell, and (3) a single compartment cell where a counter electrode with a much larger surface area than that of the working electrode is used. Also, the absorbance of this band is not shown to be functions of oxygen concentrations and applied potentials as seen in Figure 3b. The peak is almost always observed after the electrode is polarized inadvertently to a large potential. We believe that this band originates from an oxidation product of pyridine generated at the counter electrode. We have not investigated into the nature of this band further after the band was shown to arise from anodic decomposition product(s). This is perhaps the band that Slough reported from his early experiments.[9]

In order to determine the molar absorptivity and also examine effects of possible nonfaradaic processes on CVs recorded for the oxygen reduction, we conducted DCVA experiments.[15,16] In DCVA experiments, the derivative absorbance (dA/dt) signal is recorded as a function of the applied potential at a wavelength where an electrochemical product absorbs photons. The dA/dt signal is shown to be directly proportional to the faradaic current, when a reactant or product absorbing photons at a selected wavelength undergoes an electrochemical reaction. The dA/dt signal also discriminates against the nonfaradaic as well as faradaic currents, as long as reactant(s) or product(s) involved in the electrochemical reaction does not absorb photons at the wavelength selected. DCVA signals can thus be compared directly with CV currents for the calculation of molar absorptivities, if contributions from nonfaradaic processes are negligible.

In Figure 4a, the absorbance at λ_{max} (271 nm) is shown to vary during the potential scanning. Its derivative signal, i.e., DCVA, shown in Figure 4b matches well in its shape with the CV shown in Figure 1a, which was recorded concurrently with that shown in Figure 4b. The excellent agreement in shapes and corresponding potentials between DCVA and CV signals indicates that the absorption indeed results from the electrogenerated superoxide ion, and the contribution from nonfaradaic processes or impurity currents is negligible. It is interesting to note here that a very small, almost invisible, perturbation seen in the CV current at about −0.95 V is clearly seen in the DCVA as a shoulder peak. We have not investigated the nature of this small DCVA peak yet.

Figure 5 shows the DCVA curve recorded for the oxygen reduction in pyridine. While the DCVA signal is somewhat noisy, it appears to reflect the electrokinetic parameters shown by the CV in Figure 1b well in that the difference in cathodic and anodic peak potentials is comparably large as in the CV curve.

The peak CV current, i_p, follows the Randles–Cevcik expression[18]

$$i_p = 2.69 \times 10^5 n^{3/2} S D_O^{3/2} C_O^* v^{1/2} \qquad (1)$$

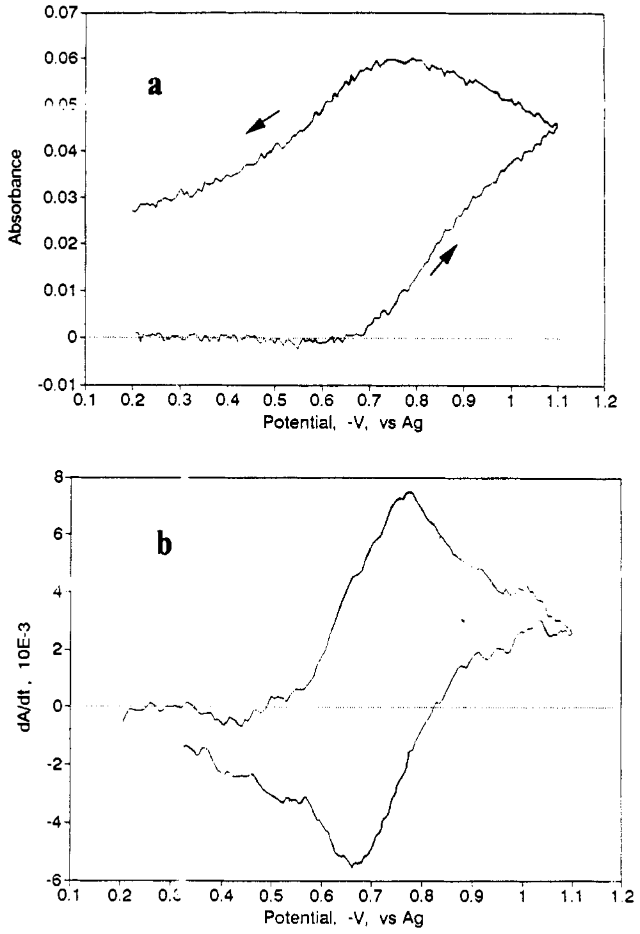

Figure 4. (a) Absorbance (A) and (b) dA/dt signals recorded at 270 nm as a function of the scanning potential. The A vs E signal was obtained simultaneously with the CV shown in Figure 1a. The dA/dt signal shown in part b was obtained by taking a derivative of the absorbance signal using 10-point smoothing of raw data.

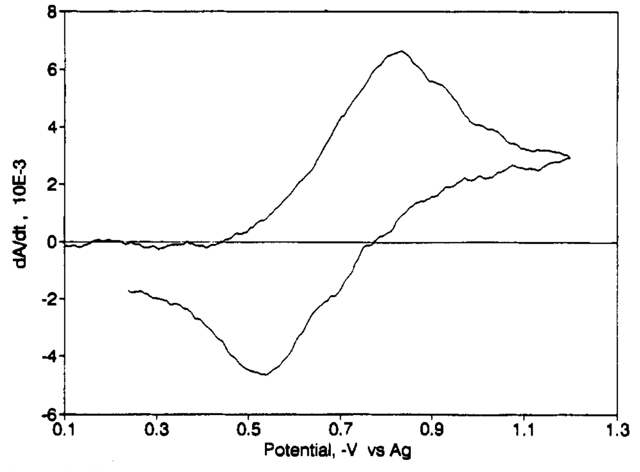

Figure 5. The dA/dt signal recorded in pyridine at 305 nm as a function of the scanning potential. This was recorded concurrently with the CV shown in Figure 1a. We used 10-point smoothing of the raw data.

where n is the number of electrons transferred, S the electrode area, D_O the diffusion coefficient of oxygen, C_O^* the oxygen concentration, and v the voltage scan rate in V/s, respectively. The corresponding DCVA expression for the NNIRS configuration is[15,16]

$$\left[\frac{dA}{dt}\right]_p = 5.58 \times 10^3 \epsilon_R n^{1/2} D_O^{1/2} v^{1/2} C_O^* \qquad (2)$$

where $[dA/dt]_p$ is the peak DCVA signal and ϵ_R is the molar

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[18] Bard A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; Chapter 6.

absorptivity of the superoxide ion. The molar absorptivity of the superoxide ion can then be obtained from the i_p and $[dA/dt]_p$ values, provided that the number of electrons transferred (n) and the electrode area (S) are known. The ϵ_{max} value thus calculated from signals recorded at various scan rates, i.e., 20, 50, and 100 mV/s, is 2006 ± 74 L·mol^{-1}·cm^{-1} in DMSO. Similarly, a value of 768 ± 58 L·mol^{-1}·cm^{-1} is obtained in pyridine. An advantage of this technique is that the concentration of the reactant, i.e., oxygen, or electrogenerated product, i.e., superoxide ion, need not be known, as both the CV and DCVA signals are recorded simultaneously.

Electrokinetic Parameters. As can be seen in CVs as well as DCVA signals shown above, electrokinetic parameters seem to be more favorable in DMSO than in pyridine. In order to obtain electrokinetic parameters quantitatively, we ran chronocoulometric and chronoabsorptometric experiments.

The chronocoulometric data for a quasireversible electron transfer reaction system has the time dependency of[19]

$$Q(t) = nFSk_fC_O^*\left(\frac{2t^{1/2}}{H\pi^{1/2}} - \frac{1}{H^2}\right) \qquad (3)$$

where F is the Faraday constant, k_f the forward rate constant for electron transfer, and t the electrolysis time. Here H has the expression

$$H = \frac{\pi^{1/2}}{2t_i^{1/2}} \qquad (4)$$

where t_i is the intercept on the time axis of the $Q(t)$ vs $t^{1/2}$ plot. One expect from these equations that k_f is found at an applied potential from the slope of the $Q(t)$ vs $t^{1/2}$ plot with H determined from the intercept. A typical $Q(t)$ vs $t^{1/2}$ plot is shown in Figure 6a for the oxygen reduction in pyridine. The k_f values thus obtained from slopes and intercepts of the $Q(t)$ vs $t^{1/2}$ plots at various applied potentials are now plotted according to the equation[20]

$$k_f = nFSk^\circ \exp\left(-\frac{\alpha nF}{RT}\eta\right) \qquad (5)$$

where k° is the exchange rate constant, α the transfer coefficient, and η the overpotential at which measurements are made. The ln (k_f) vs η plots for data obtained by chronocoulometric experiments in DMSO and pyridine are shown in Figures 7a and 8a. Since the Ag-wire pseudoreference electrode used for these measurements is not poised and thus does not hold its potential constant from experiment to experiment, we used the average value of cathodic and anodic CV peak potentials as a standard electrode potential for these plots. Standard electrode potentials reported in the literature were calculated in this way also.[4] Kinetic parameters, k° and α, evaluated from these plots in DMSO and pyridine are listed in Table I.

Chronoabsorptometric data shown in Figure 6b can be treated similarly.[21] Kinetic parameters obtained from chronoabsorptometric data are also listed in Table I. The oxygen reduction is shown to be more reversible in DMSO than in pyridine as can be seen in the table. Kinetic parameters determined by the two techniques agree well with each other within experimental errors.

Electron transfer rate constants determined in two solvents are small enough to describe the oxygen reduction as "quasireversible," as pointed out already. The difference in rate constants in these solvents, however, does not appear large enough to justify the CVs shown in Figure 1. This discrepancy may be explained by a large voltage drop due to a large uncompensated solution resistance in pyridine, as Sawyer has pointed out.[22]

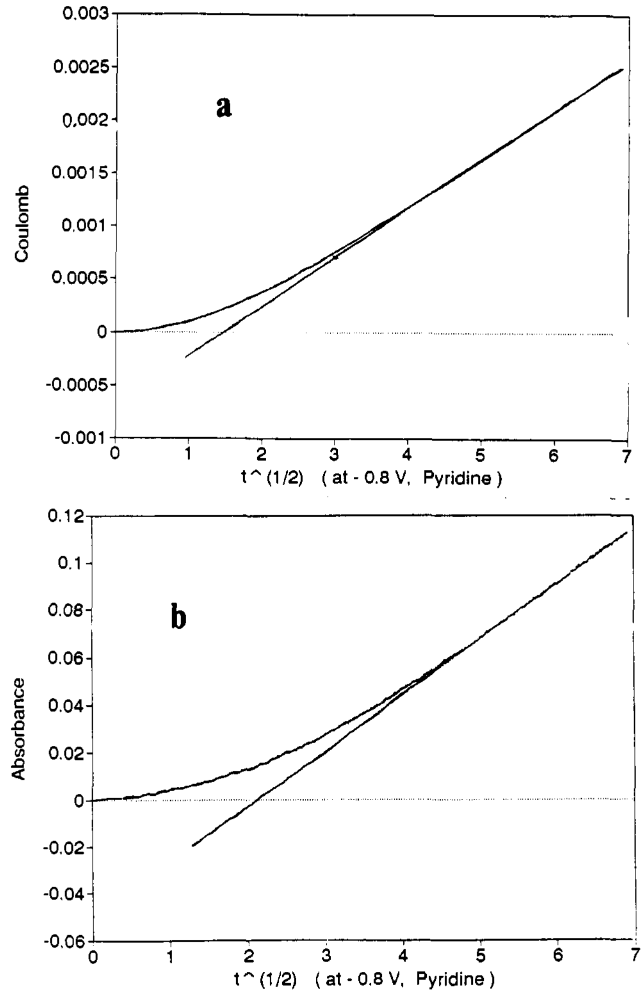

Figure 6. Chronocoulometric (a) and chronoabsorptometric (b) data for the oxygen reduction in pyridine at an applied potential of –0.80 V. The unit on the time axis is s$^{1/2}$.

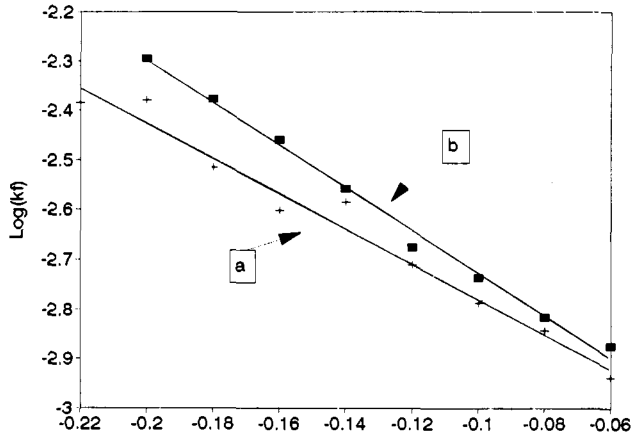

Figure 7. ln (k_f) vs η plots for data obtained from chronocoulometric (a) and chronoabsorptometric (b) experiments in DMSO.

Discussion

While the spectra reported in this work, which, to our knowledge, represent the first obtained from the electrogenerated superoxide ion, have similar spectral shapes to those reported earlier, they are red-shifted by as much as 25–65 nm compared

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(19) See Chapter 5 of ref 18.

(20) See Chapter 3 of ref 18.

(21) Bowden, E. F.; Hawkridge, F. M.; Blount, H. N. In *Electrochemical and Spectrochemical Studies of Biological Redox Complexes*; Kadish, K. M., Ed., Advances in Chemistry Series *201*, American Chemical Society: Washington, DC, 1982.

(22) See Chapter 2 of Ref 4.

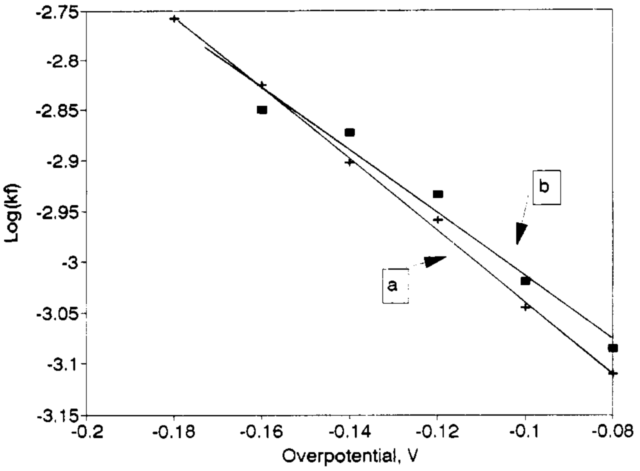

Figure 8. ln (k_f) vs η plots for data obtained from chronocoulometric (a) and chronoabsorptometric (b) experiments in pyridine.

Table I. Kinetic Parameters for Oxygen Reduction

solvent	10^4k^0, cm/s	α	techniques
DMSO	6.5	0.26	chronocoulometry
DMSO	6.0	0.26	chronoabsorptometry
pyridine	3.6	0.20	chronocoulometry
pyridine	3.4	0.20	chronoabsorptometry

to the ones reported in the literature[10-13] depending on the medium. This is perhaps because: (1) our spectra might have been recorded in more rigorously dried and purified solvents than those used in previous studies, and (2) the solvent polarity could affect the electronic transition of the superoxide ion, as is discussed below. The superoxide ion in water, as was the case in Czapski and Dorfman's work,[10,11] may contain species requiring a higher transition energy such as $HO_2^\bullet$ with its λ_{max} at 235 nm.[11] This could result in a convoluted absorption spectrum, which is blue-shifted in comparison to the pure superoxide ion. This could also have been a problem in the spectrum of potassium superoxide in DMSO[12] considering the reactivity of the superoxide ion.[1-4] Impurities and small amounts of water in DMSO might have produced secondary products such as Me_2SO_2 and thus affected the spectral shape.[12] With proton sources, such as water molecules, present in DMSO, $HO_2^\bullet$ would be produced, and its spectrum may be convoluted into the superoxide spectrum, as pointed out already. Also the presence of a supporting electrolyte in our work might have led to a lower transition energy as it affects the dielectric constant of the solution. This effect is addressed below in more detail. Finally we wish to point out that the background signal is completely subtracted in our spectra. In other words, effects of impurities have been subtracted off unless the effects result from chemical reactions of impurities with the electrogenerated superoxide ion.

Another reason for the red shifts in spectral bands in DMSO and pyridine could be due to the effect of the solvent polarity on the electronic transition. This would indicate that the superoxide ion is polar in its ground state while it could be less polar in its excited state. It is easily understandable that the superoxide ion would be quite polar in its ground state. However, the excited superoxide ion may have more of a radical than ionic characteristics, since the transition must have a π–π^* nature. Excited states produced via π–π^* transitions are generally nonpolar with radical properties.[23,24] Thus, the superoxide ion may be in a lower energy state in its ground state in DMSO than in pyridine, but the reverse may be the case in its excited state.

The difference in free energies of an ion in two solvents can be estimated from Born's solvation model.[25,26] The difference in solvation energy is calculated from Born's equation,

$$\Delta G_\pm = -\frac{Ne^2}{2}\left(\frac{1}{\epsilon_1}-\frac{1}{\epsilon_2}\right)\left(\frac{Z_+^2}{r_+}-\frac{Z_-^2}{r_-}\right) \qquad (6)$$

where N is the Avogadro number, e the electron charge, r the radius of ions, Z the ionic charge, and ϵ the dielectric constants of two solvents. With radii of superoxide and tetra-*n*-butylammonium ions of 1.76 and about 10 Å and dielectric constants of 7.48 and 46.6 for pyridine and DMSO,[27] the difference in solvation energy of about 0.47 eV can be calculated from equation 6 for two solvents. This explains most of the spectral shift, which amounts to about 0.51 eV from 271 nm in DMSO and 305 nm in pyridine. Although the excited state of the superoxide ion is expected to be less polar for the reason speculated above, it does not appear to affect the spectral shift as much. This suggests that the excited superoxide ion may be almost as polar as the ground state. The difference in solvation energies may also explain the difference in electrode kinetics in two solvents as well, since Marcus' reorganization energy of the electrogenerated superoxide ion is affected by the dielectric constant of the solvent.[28]

We believe that our ϵ_{max} values represent more accurate ones than those reported earlier, since the concentration of the superoxide ion or oxygen is not taken into account for its calculation. The purity of commercially available potassium superoxide is relatively low at about 96%, which decays over time due to water, SO_2, and other impurities present in DMSO. For this reason, Matheson and Lee also pointed out in their report[12] that the superoxide ion concentration could be lower than they had originally prepared from potassium superoxide by as much as 30% and gave an upper limit of 1,500 $L\cdot mol^{-1}\cdot cm^{-1}$ for the molar absorptivity.

The more difficult question concerning our observation is, however, why molar absorptivities are so much different in the two solvents studied here. We speculate that superoxide ions could form ion pairs with quaternary ammonium ions in nonpolar pyridine, which may displace the potential surface of the superoxide ion on the potential axis in the ground state. This could result in a lower Frank–Condon probability for the electronic transition in pyridine compared to that in DMSO. A more systematic study on the effects of other solvents and electrolytes on the transition energy of the superoxide ion is currently underway to investigate the nature of the potential surface.

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Registry No. DMSO, 67-68-5; O_2, 7782-44-7; Bu_4NClO_4, 1923-70-2; superoxide, 11062-77-4; pyridine, 110-86-1.

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