Electrochemistry of oxygen and superoxide ion in dimethylsulfoxide at platinum, gold and mercury electrodes

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ELECTROCHEMISTRY OF OXYGEN AND SUPEROXIDE ION IN DIMETHYLSULFOXIDE AT PLATINUM, GOLD AND MERCURY ELECTRODES

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The electrochemical behavior of dissolved oxygen in aqueous solutions at various electrodes has been of interest to our group for some time[1-3]. Studies have been made of the effect of electrode material, electrode pre-conditioning, supporting electrolyte, and solution pH upon the kinetics and the mechanisms for the reduction process. However, the effect of solvent has not been evaluated in these earlier studies. Because the reduction products of oxygen are either peroxide or water, the protic character of the solvent should have a significant influence upon the electrochemistry. KOLTHOFF AND REDDY[4] first noted the characteristics of the polarographic reduction of oxygen in dimethylsulfoxide (DMSO).

The present discussion summarizes the results of a detailed investigation of the electrochemical behavior of oxygen and superoxide ion at several different electrodes using dimethylsulfoxide as a solvent. This solvent provides an aprotic system that is distinctly different from aqueous systems and gives a means of studying the effect of solvent upon the electrochemistry of dissolved oxygen. During the course of this research, two publications have appeared that discuss some aspects of the electrochemistry of oxygen in DMSO[5,6]. Both present evidence that the reduction product in aprotic solvents is superoxide ion produced by a one-electron process. In both cases, the conclusion is based on cyclic voltammetry and the observation of an e.s.r. signal for the reduction product. The conclusion that the reduction process is one-electron is based either on a slope analysis of the reduction polarogram[6] or on the peak potentials for the cyclic curves[5], assuming a quasi-reversible reaction.

EXPERIMENTAL

Electrochemical measurements were made using an instrument constructed from Philbrick operational amplifiers. The design of this instrument and the details of its performance have been described by DEFORD[7]. Electrolysis currents up to 20 mA could be used with an error of less than $\pm 0.1\%$. Potential–time curves were recorded with a Sargent SR stripchart recorder using a chart speed of 12 in./min. The recorded voltages were accurate to ± 0.005 V. Integration of the current–time curves resulting from controlled-potential electrolysis was accomplished with an electronic integrator based on operational amplifiers[7]; the integrals were measured with an error of less than $\pm 0.3\%$.

A Leeds and Northrup coulometric cell was used for both the voltammetric

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and the chronopotentiometric studies. All measurements used a three-electrode configuration with a Ag/AgCl reference electrode in aqueous 1 F (CH$_3$)$_4$NCl. The junction between the reference electrode and the sample solution was accomplished by sealing a soft glass bead in the end of a piece of borosilicate glass tubing; this gave a junction with a leak rate of less than 2 μl/h. To minimize iR effects and the diffusion of water into the cell solution, the reference electrode was placed in a Luggin capillary filled with the sample solution. The internal resistance of the reference electrode plus Luggin capillary was about 450 kΩ. The potential of the Ag/AgCl reference electrode *versus* an aqueous saturated calomel electrode (S.C.E.) was ± 5 mV; for this reason the potentials reported here are given relative to the S.C.E. A shielded platinum-foil electrode served as the counter electrode.

A platinum working electrode consisted of a Beckman inlay electrode which had been polished with 800-mesh alumina to a bright mirror finish. The mercury working electrode was prepared by amalgamating another Beckman platinum inlay electrode after first abrading its surface with carborundum paper, 400 grit. The surface was renewed periodically by gentle abrasion of the surface followed by renewal of the mercury surface. The gold working electrode was prepared by sealing a 0.45-cm gold rod into a polyethylene tube, grinding the gold surface flat with the end of the tube, and then polishing the gold surface with progressively finer grades of alumina, finishing with 800 mesh. The electrode areas were calculated from measurements of their mean diameter with a cathetometer.

A gas-tight coulometric cell was constructed from a 40/35 standard taper, borosilicate glass joint. The top of the cell was fitted with a tube the end of which was closed with a fine glass frit to isolate the platinum foil counter electrode, a 7/15 standard taper joint to accommodate the reference electrode, and a 7-mm tube closed at the top with a rubber serum cap through which the solution could be saturated with gas by inserting a syringe needle. Also, gas-saturated solution could be injected into the sealed cell through the serum cap with a hypodermic syringe so that the cell was completely filled without residual bubbles or air space.

A platinum wire was sealed into the bottom of the cell to provide electrical contact with a mercury pool working electrode. A cylindrical platinum-gauze electrode could be used in place of the mercury pool as a working electrode. The total internal volume of the cell was 43 ml. The cell solution was stirred magnetically using a Teflon-coated stirring bar. For some measurements, the counter electrode was isolated in a second tube closed with a fine glass frit to prevent contamination of the cell solution. All cells and glassware were dried in an oven before use. The coulometric cell was used to prepare known concentrations of superoxide ion using a control potential of -1.00 V *vs.* S.C.E.

Electrolyte solutions were prepared from J. T. Baker and Company reagent-grade dimethylsulfoxide; this material had a specified water content of 0.001%. Tetraethylammonium perchlorate (Eastman Kodak) and ammonium perchlorate (G. F. Smith and Co.) were used as supporting electrolytes. Both were recrystallized once from water, dried, and stored in a desiccator. Oxygen from the Liquid Carbonic Division of General Dynamics and pre-purified nitrogen from Airco Company were used as received.

The solubility of oxygen in 0.10 F (Et)$_4$NClO$_4$–DMSO was determined by a modification of the Winkler method in which the manganese dioxide formed by

reaction of O_2 with $Mn(II)$ was titrated with $Fe(II)$[8]. The procedure was modified so that the final solution contained 10 ml of 0.1 F $(Et)_4NClO_4$ in DMSO/80 ml of solution. Thus, the titration of a sample of O_2-saturated distilled water, which served as a standard, was carried out as nearly as possible under the same conditions as the titration of the O_2-saturated DMSO sample. The value used for the solubility of O_2 in H_2O at 25° was[9] 1.228×10^{-3} M. This value, corrected for barometric pressure, was multiplied by the ratio of the $Fe(II)$ titrant volumes for the DMSO sample and the H_2O sample, respectively, to give the value of the solubility of O_2 in 0.10 F $(Et)_4NClO_4$–DMSO solutions. The sample volumes were adjusted to consume approximately equal amounts of titrant (20 ml for the H_2O sample; 10 ml for the DMSO sample). This procedure was used to cancel errors inherent in the absolute Winkler oxygen determination.

RESULTS

The voltammetric reduction of oxygen in 0.05 F $(Et)_4NClO_4$–DMSO solution at platinum and mercury electrodes is illustrated by Fig. 1. With the platinum
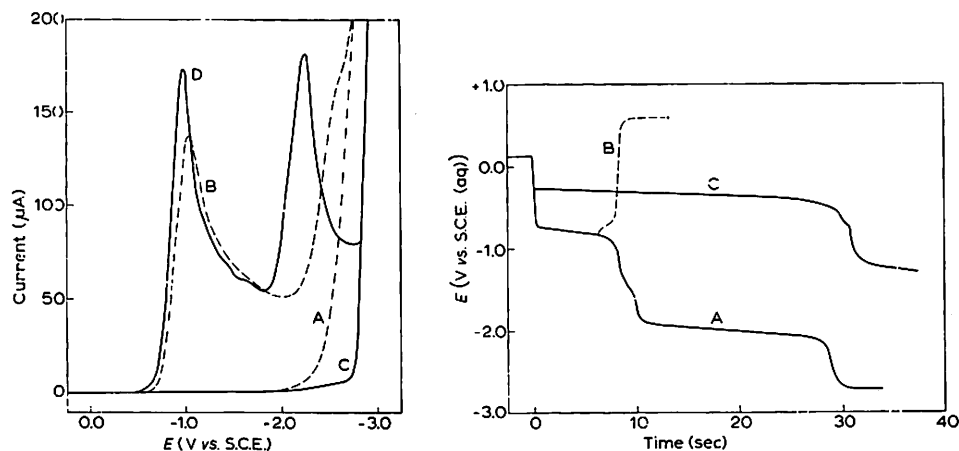

Fig. 1. Voltammetric reduction of oxygen in dimethylsulfoxide with 0.05 F Et_4NClO_4 as supporting electrolyte. Electrode area: Pt, 0.233 cm²; Hg(Pt), 0.210 cm². Scan rate, 0.10 V/sec; solns. satd. with gas at 1 atm. (oxygen concn., 2.1×10^{-3} F). (A), Pt, N_2; (B), Pt, O_2; (C), Hg(Pt), N_2; (D), Hg(Pt), O_2.

Fig. 2. Chronopotentiometric reduction of oxygen in DMSO solns. at a mercury electrode. (A), 0.10 F Et_4NClO_4 supporting electrolyte; (C), 0.10 F NH_4ClO_4 supporting electrolyte; (B), the reverse chronopotentiogram of curve A ($\tau_f/\tau_r = 3$). Current, 0.080 mA; electrode area, 0.210 cm²; oxygen concn.; 2.10×10^{-3} F.

electrode (Curve B) a single reduction peak is observed (peak potential, -1.05 V) plus a shoulder on the solvent reduction break at -2.6 V. In contrast, the mercury electrode gives two well-defined reduction peaks for oxygen (Curve D) with peak potentials of -0.97 V and -2.25 V.

The chronopotentiometric behavior of oxygen in DMSO solutions at a mercury electrode is shown in Fig. 2. Curve A is for 0.1 F $(Et)_4NClO_4$ and indicates that the same number of electrons are involved in each step of a two-step reduction ($\tau_2/\tau_1 = 3$). Curve B is the reverse chronopotentiogram of Curve A; this gives a transition time

ratio of 1:3 and indicates that both the forward and reverse processes are diffusion-controlled. Curve C represents the reduction of oxygen when the supporting electrolyte is 0.1 F NH_4ClO_4 instead of $(Et)_4NClO_4$. The reduction occurs at much more positive potentials and the transition time is four times as great as for the first reduction step of Curve A. This implies that twice as many electrons are involved in this reduction step as in each step of Curve A. Chronopotentiometry of oxygen with a gold electrode gives an almost identical set of curves to those for a mercury electrode (Fig. 2). With a platinum electrode, a similar set of curves is obtained, except that the second reduction step for oxygen (Curve A, Fig. 2) is not observed. This is similar to its behavior with voltammetric measurements (Curve B, Fig. 1). The chronopotentiometric behavior of oxygen in DMSO with three different electrode materials is summarized in Table 1. The chronopotentiometric constant for the NH_4ClO_4 solution is essentially twice as large as for the $(Et)_4NClO_4$ solution, which indicates that twice as many electrons are involved in the reduction step.

TABLE 1

CHRONOPOTENTIOMETRIC REDUCTION OF OXYGEN IN DMSO SOLUTIONS

Oxygen concn. = 2.10×10^{-3} F; $t = 25 \pm 0.5°$. Electrode areas: Pt, 0.233 cm²; Au, 0.162 cm²; Hg(Pt), 0.210 cm².

	i (mA)	$i\tau^{\frac{1}{2}}$ $(mA\ sec^{\frac{1}{2}})$	$i\tau^{\frac{1}{2}}/AC$ $(A\ sec^{\frac{1}{2}}\ cm\ mole^{-1})$
I. 0.10 F $(Et)_4NClO_4$			
A. Pt electrode	0.140	0.218	
	0.100	0.222	
	0.070	0.224	
	0.050	0.228	
	0.040	0.238	
	Av. 0.226		462
B. Au electrode	0.110	0.165	
	0.080	0.165	
	0.050	0.171	
	0.040	0.173	
	0.035	0.177	
	Av. 0.170		500
C. Hg(Pt) electrode	0.140	0.227	
	0.100	0.220	
	0.070	0.220	
	0.050	0.223	
	Av. 0.222		504
II. 0.10 F NH_4ClO_4			
A. Hg(Pt) electrode	0.200	0.418	
	0.160	0.418	
	0.120	0.418	
	0.080	0.425	
	Av. 0.420		953

For definitely establishing the number of electrons involved in the reduction of oxygen in 0.1 F Et_4NClO_4 solutions, controlled-potential coulometric reductions have been made using known amounts of oxygen. Thus, the number of electrons/oxygen molecule is determined directly for a given reduction potential. The results of this study are summarized in Table 2 for both mercury and platinum electrodes. With a control potential of -1.00 V, the average for three runs at a platinum electrode is 1.07 electrons/oxygen molecule and for two runs at a mercury electrode is 1.26

electrons. With the control potential set at -2.40 V using a mercury electrode, 2.08 electrons/oxygen molecule are consumed.

TABLE 2

CONTROLLED POTENTIAL REDUCTION OF OXYGEN IN 0.1 F (Et)$_4$NClO$_4$ SOLUTIONS OF DMSO

Oxygen concn. = 2.10 $\times$ 10^{-3} F, t = 25 $\pm$ 0.5°.

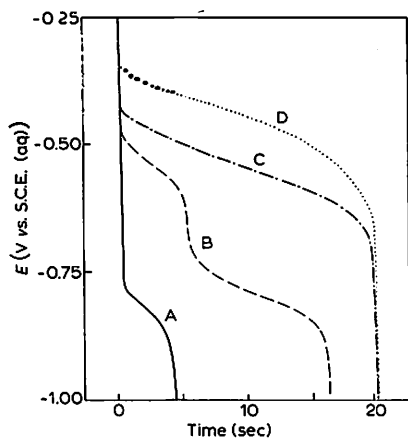| Control potential, (V vs. S.C.E. (aq))	Electrode	n (No. of electrons/O$_2$)
-1.00	Pt gauze	1.14
-1.00	Pt gauze	1.01
-1.00	Pt gauze	1.06
		Av. 1.07
-1.00	Hg pool	1.36
-1.00	Hg pool	1.17
		Av. 1.26
-2.40	Hg pool	2.08

Fig. 3. Chronopotentiometric reductions of oxygen in DMSO solns. of 0.1 F Et$_4$NClO$_4$ with added amounts of NH$_4$ClO$_4$. (A), no NH$_4$ClO$_4$; (B), 5.6 $\times$ 10^{-3} F NH$_4$ClO$_4$; (C), 11.1 $\times$ 10^{-3} F NH$_4$ClO$_4$; (D), 29.2 $\times$ 10^{-3} F NH$_4$ClO$_4$. Current, 0.10 mA; electrode area, 0.210 cm^2; oxygen concn., 2.10 $\times$ 10^{-3} F.
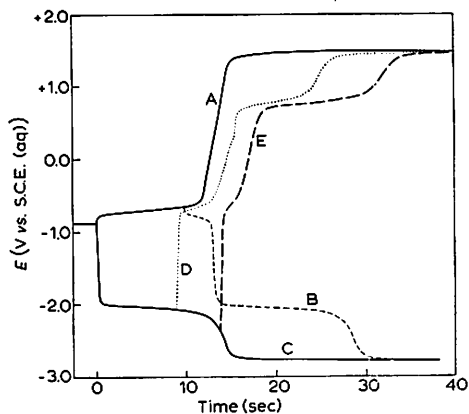
Fig. 4. Chronopotentiometric oxidation and reduction of superoxide ion in DMSO solns. of 0.10 F (Et)$_4$NClO$_4$ at a gold electrode. (A), oxidation; (B), reverse chronopotentiogram of curve A; (C), reduction; (D and E), reverse chronopotentiograms of curve C. Current, 0.070 mA; electrode area, 0.162 cm^2; superoxide ion concn., 5.34 $\times$ 10^{-3} F.

The effect of added protons, in the form of NH$_4$ClO$_4$, upon the reduction chronopotentiogram of oxygen is shown by Fig. 3. Curve A is the first step reduction of oxygen in 0.1 F Et$_4$NClO$_4$ while Curves B, C, and D represent the effect of adding NH$_4$ClO$_4$ to give concentrations of 5.6 $\times$ 10^{-3} F, 11.1 $\times$ 10^{-3} F, and 29.2 $\times$ 10^{-3} F, respectively. The transition time, τ, reaches its maximum value when the ratio of concentrations for the NH$_4^+$ ion relative to O$_2$ attains a value of about 5. Below this value, two waves are observed. The potential for the first is dependent upon the NH$_4$ClO$_4$ concentration, but the second wave occurs at the same potential as observed for Curve A (no NH$_4$ClO$_4$). Thus, this latter process is probably the one-electron

reduction of oxygen, while the first wave of Curve B is indicative of the two-electron process, as are Curves C and D. A similar set of results is obtained if HNO_3 is used in place of NH_4ClO_4, and also if a platinum electrode is used instead of a mercury electrode.

The chronopotentiometric behavior of superoxide ion is illustrated in Fig. 4. Curve A represents the oxidation of the ion back to oxygen, and Curve B is the reverse chronopotentiogram. The first part of the latter curve represents the reduction of oxygen ($\tau_r/\tau_f = 1/3$) while the transition at approximately -2.0 V is for the reduction of superoxide ion left unoxidized at the electrode surface when the current was reversed. The reduction of superoxide ion to peroxide ion is shown by Curve C with Curves D and E indicating current reversals at different times on the reduction wave. In the case of Curve D, the first transition is due to unreduced superoxide ion at the electrode surface and the second transition is for the oxidation of peroxide ion to oxygen (a two-electron process). Curve E is for the reverse chronopotentiogram at the transition time for the reduction wave; there is a small amount of superoxide ion indicated plus an extensive wave for the oxidation of peroxide ion to oxygen. The long transition time for the latter is due to the two-electron process and to the migra-

TABLE 3

CHRONOPOTENTIOMETRIC OXIDATION AND REDUCTION OF SUPEROXIDE ION IN 0.1 F (Et)$_4$NClO$_4$ SOLUTIONS OF DMSO

Superoxide concn. = 5.34×10^{-3} F; $t = 25 \pm 0.5°$; N$_2$-satd.; Electrode areas: Pt, 0.233 cm^2; Au, 0.162 cm^2; Hg(Pt), 0.210 cm^2.

	i (mA)	$i\tau^{\frac{1}{2}}$ (mA sec$^{\frac{1}{2}}$)	$i\tau^{\frac{1}{2}}/AC$ (A sec$^{\frac{1}{2}}$ cm mole^{-1})
I. Oxidation			
A. Pt Electrode	0.140	0.335	
	0.110	0.337	
	0.070	0.342	
		Av. 0.338	272
B. Au Electrode	0.110	0.243	
	0.090	0.243	
	0.070	0.244	
	0.060	0.246	
		Av. 0.244	282
C. Hg(Pt) Electrode	0.200	0.260	
	0.140	0.283	
	0.090	0.284	
	0.060	0.289	
		Av. 0.279	249
II. Reduction			
A. Au Electrode	0.120	0.252	
	0.080	0.255	
	0.060	0.261	
		Av. 0.256	296
B. Hg(Pt) Electrode	0.200	0.306	
	0.140	0.359	
	0.100	0.347	
		Av. 0.337	300

tion of superoxide into the electrode during the course of the reverse chronopotentio-
gram. Curves D and E establish that superoxide ion is significantly easier to oxidize,
by about 1.5 V, than is peroxide ion. Table 3 summarizes the chronopotentiometric
data for the oxidation and reduction of superoxide ion at platinum, gold, and mercury
electrodes. The data confirm that the electrode reactions are diffusion-controlled and
that superoxide ion concentrations can be determined chronopotentiometrically.
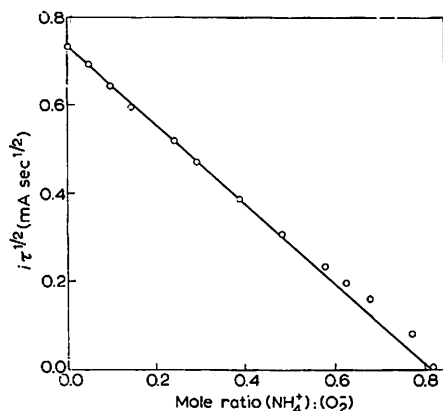

Fig. 5. Chronopotentiometric titration of superoxide ion with NH_4ClO_4 in 0.10 F $(Et)_4NClO_4$–DMSO
soln. Original conditions, 1.04×10^{-3} moles of O_2^- in 83 ml of soln.; titrant, 0.495 F NH_4ClO_4.
Amount of released oxygen (determined chronopotentiometrically); 0.71 mole/mole of NH_4ClO_4
added.

The chronopotentiometric oxidation wave for superoxide ion has provided a
means for determining the effect of the addition of ammonium perchlorate on the
superoxide ion concentration. Fig. 5 indicates the anodic $i\tau^{\frac{1}{2}}$ product for superoxide ion
as a function of added NH_4^+ ion; the zero intercept occurs at a mole ratio for NH_4^+
to O_2^- of 0.81. That the ratio is less than unity, is probably due, in part, to the slow
spontaneous decomposition of superoxide ion to oxygen and peroxide ion. This occurs
at a rate of 1–3%/h under the conditions of the experiments. The amount of oxygen
produced when the intercept is at zero has been determined chronopotentiometrically
to be 0.57 mole/mole of superoxide ion. This corresponds to 0.71 mole of oxygen/mole
of NH_4^+ used in the titration. These results, plus their interpretation, are summarized
in Table 6.

If $LiClO_4$ is used as a supporting electrolyte with a mercury electrode, then the
reduction of oxygen in DMSO gives evidence of some type of film formation. The
product $i\tau$ is approximately constant for this system and the transition time for the
reverse chronopotentiogram is essentially equal to the forward transition time. Also,
after one chronopotentiometric reduction of oxygen at this electrode, a second re-
duction is blocked until the surface is renewed or reoxidized. The film may consist of
LiO_2 on the surface of mercury. No reduction is observed for this electrolyte–electrode
system in the absence of oxygen.

DISCUSSION AND CONCLUSIONS

On the basis of the data in Table 2, oxygen, in aprotic systems, is reduced by

a one-electron process to superoxide ion. The latter species is relatively stable and decomposes slowly at millimolar concentrations to peroxide ion and oxygen (less than 3%/h).

By using the data of Tables 1 and 3, the diffusion coefficients for oxygen and for superoxide ion in 0.1 F $(Et)_4NClO_4$ solutions of DMSO can be evaluated. The calculated values, based on the average of the data presented in the two tables, are: $D_{O_2} = 3.23 \times 10^{-5}$ cm^2 sec and $D_{O_2^-} = 1.08 \times 10^{-5}$ cm^2 sec. That the diffusion coefficient for the superoxide ion in DMSO is three times smaller than it is for oxygen is surprising and indicates that there is either extensive solvation of the ion or that ion pairs are formed with the supporting electrolyte cations. Both processes probably hinder the diffusion of the superoxide species.

Consideration of a number of chronopotentiograms for both the reduction of oxygen and the oxidation of superoxide ion has verified that both reactions are irreversible. Plots of E vs. log $[1 - (t/\tau)^{\frac{1}{2}}]$ always give linear curves. The results of the latter type of analysis for chronopotentiograms obtained under a variety of conditions are summarized in Table 4. In addition, the quarter-wave potential, $E_{\frac{1}{4}}$, for the chronopotentiograms is tabulated. If the reactions were truly reversible then the values for $E_{\frac{1}{4}}$ for both the reduction of O_2 and the oxidation of O_2^- should be the same. In the case of the platinum electrode, the difference is 0.075 V and for the mercury electrode it is 0.197 V. The right-hand column of Fig. 4 summarizes the extrapolated potentials at time equal to zero for the chronopotentiograms. This is obtained from the irreversible logarithmic plot. From the slope of such plots, the value of αn_a can be evaluated; the results are tabulated in Table 4.

For irreversible chronopotentiometric systems, DELAHAY AND BERZINS[10] have developed expressions for evaluating kinetic parameters both for reduction processes

$$E = \frac{2.3\,RT}{\alpha n_a F} \log \frac{nFAC^0 k_{f,h}^0}{i} + \frac{2.3\,RT}{\alpha n_a F} \log \left[1 - \frac{t^{\frac{1}{2}}}{\tau^{\frac{1}{2}}}\right] \tag{1}$$

and for oxidation processes

$$E = \frac{-2.3\,RT}{(1-\alpha)n_a F} \log \frac{nFAC^0 k_{b,h}^0}{i} - \frac{2.3\,RT}{(1-\alpha)n_a F} \log \left[1 - \frac{t^{\frac{1}{2}}}{\tau^{\frac{1}{2}}}\right] \tag{2}$$

TABLE 4

ANALYSIS OF CHRONOPOTENTIOMETRIC REDUCTION WAVES FOR OXYGEN AND OXIDATION WAVES FOR SUPEROXIDE ION IN 0.1 F $(Et)_4NClO_4$ SOLUTIONS OF DMSO

Oxygen concn. = 2.10 × 10^{-3} F; t = 25 ± 0.5°. Electrode areas: Pt, 0.233 cm^2; Au, 0.162 cm^2; Hg(Pt), 0.210 cm^2.

	Slope E vs. log$(1-(t/\tau)^{\frac{1}{2}})$	i (mA)	αn_a	$E_{\frac{1}{4}}$ (V vs. S.C.E.)	$E(t=0)$ (V vs. S.C.E.)
I. O_2 Reduction					
A. Pt electrode	0.094	0.050	0.63	−0.779	−0.751
B. Au electrode	0.148	0.035	0.40	−0.783	−0.739
C. Hg(Pt) electrode	0.125	0.050	0.47	−0.786	−0.745
II. O_2 Reduction, 0.05 F NH$_4$ClO$_4$					
A. Hg(Pt) electrode	0.161	0.100	0.37	−0.359	−0.311
III. O_2^- Oxidation ([O_2^-] = 2.0 · 10^{-3} F)					
A. Pt electrode	0.112	0.070	0.53	−0.704	−0.736
B. Hg(Pt) electrode	0.173	0.050	0.34	−0.589	−0.632

where E is the potential of the working electrode *vs.* the normal hydrogen electrode (N.H.E.), α the transfer coefficient for the reduction process, n_a the number of electrons in the rate-determining charge transfer step, A the electrode area, F the faraday, R the gas constant, T the absolute temperature, C^0 the concentration of the electroactive species in the bulk of the solution, τ the transition time, t the time of electrolysis, and $k_{f,h}{}^0$ and $k_{b,h}{}^0$ the heterogeneous rate constants for the reduction and oxidation reactions, respectively. The right-hand terms of these two expressions are the basis for the data of Table 4.

The data of Table 4 together with eqns. (1) and (2) permit evaluation of the kinetic parameters for the reduction of oxygen and for the oxidation of superoxide ion, both in DMSO. The results of such evaluations are summarized in Table 5. However, the heterogeneous rate constants, $k_{f,h}{}^0$ and $k_{b,h}{}^0$, are only meaningful in a comparative sense if they are converted to the simple heterogeneous constant, $k_{s,h}{}^0$ by the expression[11],

$$k_{s,h}{}^0 = k_{f,h}{}^0 \exp[-\alpha n_a F E^0/RT] \tag{3}$$

$$k_{s,h}{}^0 = k_{b,h}{}^0 \exp[(1-\alpha)n_a F E^0/RT] \tag{4}$$

TABLE 5

KINETIC PARAMETERS FOR THE ELECTROCHEMISTRY OF OXYGEN AND SUPEROXIDE ION IN 0.1 F (Et)$_4$NClO$_4$ SOLUTIONS OF DMSO

Assume $E^0 = -0.501$ V *vs.* N.H.E.

	Electrode	E(t=0) (V vs. N.H.E.)	αn_a	log $k_{f,h}{}^0$	log $k_{s,h}{}^0$
A. Reduction of O$_2$	Pt	−0.509	0.63	−8.401	−3.056
	Au	−0.497	0.40	−6.334	−2.947
	Hg(Pt)	−0.503	0.47	−6.930	−2.949
			$(1-\alpha)n_a$	log $k_{b,h}{}^0$	
B. Oxidation of O$_2^-$	Pt	−0.494	0.53	+1.617	−2.878
	Hg(Pt)	−0.390	0.34	+0.480	−2.400
			αn_a		
C. Combined data	Pt		0.55		−2.942
averaged	Hg(Pt)		0.56		−3.390

where E^0 is the standard electrode potential for the electrode reaction. Because the values for $E_{(t=0)}$ at the platinum electrode differ by only 0.015 V for the reduction and oxidation reactions, a reasonable value for E^0 is −0.501 V. The simple heterogeneous rate constant, $k_{s,h}{}^0$, has been evaluated using this value for E^0; the values are summarized in the right column of Table 5. By equating eqns. (3) and (4) in terms of E^0, the value of $k_{s,h}{}^0$ can be determined without assuming a value for E^0. The bottom right-hand values in Table 5 have been evaluated in this way using the averaged values for αn_a and $(1-\alpha)n_a$. Considering the data of Table 5, the average values for the kinetic parameters are: $\alpha n_a = 0.55$ and $k_{s,h}{}^0 = 10^{-3}$. Within the expected experimental error, the processes for oxygen reduction and superoxide ion oxidation appear to be independent of electrode material.

The data presented in Fig. 4 indicate the behavior of superoxide ion under both cathodic and anodic conditions. Thus, the O$_2^-$ species is oxidized to oxygen at −0.73 V *vs.* S.C.E. and reduced to peroxide ion at −2.02 V *vs.* S.C.E. The peroxide

ion produced is oxidized directly to oxygen when the current is reversed; this occurs at $+0.75$ V vs. S.C.E. Hence, peroxide ion is not oxidized to superoxide ion on the basis of the observed data.

The data from Fig. 5 are included in Table 6 together with a summary of the other analytical results from the experiment. This table also indicates the expected mole ratios for two different disproportionation reactions. The experimental results support the conclusion that the major part of the superoxide ion goes to hydrogen peroxide and oxygen upon the addition of hydrogen ion. Apparently, some of the peroxide is formed as the HO_2^- species also.

TABLE 6

ANALYSIS OF DATA FOR PROTON-INDUCED DISPROPORTIONATION OF SUPEROXIDE ION

|	Molar ratios		
	Assuming $H^+ + 2O_2^- \rightarrow HO_2^- + O_2$	Assuming $2H^+ + 2O_2^- \rightarrow H_2O_2 + O_2$	Experimental results
O_2 produced/O_2^-	0.50	0.50	0.57
NH_4^+ required/O_2^-	0.50	1.00	0.81
O_2 produced/NH_4^+	1.00	0.50	0.71

The electrochemistry of oxygen and its reduction products in DMSO solutions can be summarized by the equations (formal potentials are given vs. S.C.E.):

$$O_2 + e^- \rightarrow O_2^-, \qquad E' = -0.75 \text{ V} \tag{5}$$

$$O_2^- + e^- \rightarrow O_2^{2-}, \qquad E' = -2.02 \text{ V} \tag{6}$$

$$O_2^- \rightarrow O_2 + e^-, \qquad E' = -0.73 \text{ V} \tag{7}$$

$$O_2^{2-} \rightarrow O_2 + 2\,e, \qquad E' = +0.75 \text{ V} \tag{8}$$

The reaction expressed by eqn. (6) is not observed with a platinum electrode but is with gold and mercury electrodes. In the presence of a proton source, a rapid disproportion reaction occurs

$$2\,O_2^- + 2\,H^+ \rightarrow H_2O_2 + O_2 \tag{9}$$

In the presence of 0.1 F NH_4ClO_4 (Fig. 2), oxygen is apparently reduced directly to hydrogen peroxide, with the potential for the reaction dependent upon the proton concentration (Fig. 3).

$$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2, \qquad E' = -0.28 \text{ V} \tag{10}$$
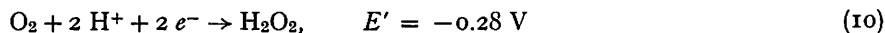
This reaction, or its equivalent, becomes the predominant electrode reaction when the NH_4^+ ion concentration is at least five times the oxygen concentration as illustrated by Fig. 3. An alternative and more plausible mechanism that leads to the overall reaction expressed by eqn. (10) is to have as the primary reduction step, that which is indicated by eqn. (5). In the presence of a proton source, the superoxide ion reacts rapidly with a proton to give a highly unstable protonated superoxide

$$O_2^- + H^+ \rightarrow HO_2 \tag{11}$$

The latter disproportionates extremely rapidly to give hydrogen peroxide and oxygen

$$2\ HO_2 \rightarrow H_2O_2 + O_2 \tag{12}$$

the oxygen being reduced by the reaction of eqn. (5). The process indicated by eqn. (11) would bring about the positive shift of the reduction potential with increasing proton concentrations (Fig. 3). The combination of eqns. (5), (11), and (12) leads to the overall reduction process indicated by eqn. (10). Such a combination of reactions is consistent with the mechanisms for oxygen reduction in water that have been proposed by KORYTA[12]. Thus, a plausible mechanism for oxygen reduction under all solvent conditions is a primary one-electron step to superoxide ion which, in the presence of protic solvents, disproportionates to oxygen and hydrogen peroxide (eqns. (11) and (12)).

SUMMARY

The electrochemistry of dissolved oxygen and of superoxide ion in dimethylsulfoxide solutions has been studied at platinum, gold and mercury electrodes using voltammetric and chronopotentiometric techniques as well as controlled-potential coulometry. In the absence of protic electrolytes and solvents, oxygen is reduced in two one-electron steps, first to superoxide ion at a potential of -0.75 V vs. S.C.E. and then to peroxide ion at a potential of -2.02 V vs. S.C.E. The second step is not observed with a platinum electrode. Superoxide ion is oxidized to oxygen at -0.73 V and is reduced to peroxide ion at -2.02 V. Peroxide ion is oxidized directly to oxygen at $+0.75$ V by a two-electron process. In the presence of a protic electrolyte (0.1 F NH_4ClO_4) oxygen is reduced in one step to hydrogen peroxide at -0.28 V.

The kinetic parameters for the oxygen–superoxide ion electrode reaction are essentially the same for all three electrodes; the average for all determinations is: $\alpha n_a = 0.55$; $k_{s,h}{}^0 = 10^{-3}$. The diffusion coefficients for oxygen and superoxide ion in 0.1 F (Et$_4$)NClO$_4$–DMSO solutions have been evaluated; $D_{O_2} = 3.23 \cdot 10^{-5}$ cm^2 sec and $D_{O_2^-} = 1.08 \cdot 10^{-5}$ cm^2 sec. Mechanisms are proposed for the electrode reactions and for disproportionation reactions that are consistent with the observed experimental data.

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Correction to eg (12), p. 100 mechanism

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"Mechanism of Superoxide Disproportionation in Aprotic Solvents"

$$O_2 + e^- \rightleftharpoons O_2^{\cdot -} \qquad \times 2$$

$$O_2^{\cdot -} + HA \rightleftharpoons HO_2^{\cdot} + A^-$$

$$HO_2^{\cdot} + O_2^{\cdot -} \longrightarrow HO_2^- + O_2$$

$$HO_2^- + HA \longrightarrow H_2O_2 + A^-$$

$$Net: \quad 2O_2 + 2e^- + 2HA \longrightarrow H_2O_2 + O_2 + 2A^-$$