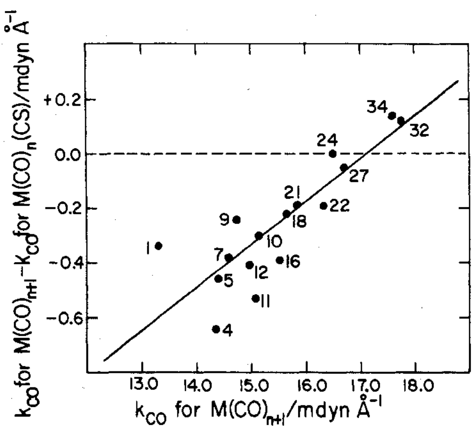

Figure 3. Plot of the difference in CO stretching force constants for $M(CO)_{n+1}$ and $M(CO)_n(CS)$ vs. CO stretching force constant for $M(CO)_{n+1}$.

spectra[5] are undoubtedly due in part to the operation of this effect in the π-electron-deficient, 17-electron complexes produced on ionization.

The conflicting descriptions of thiocarbonyl bonding reported by previous workers is a direct consequence of the crossover in CS and CO electronic properties. When $k_{\rm CO}[M(CO)_{n+1}] < 17.1$ mdyn/Å, the π-acceptor to (σ + π)-donor ratio is greater for CS than for CO. This is in agreement with the infrared spectra of $CpMn(CO)_2(CS)$[6,7] and $[CpMn(CS)(NO)L]^+$ [9] and ^{13}C NMR spectra of $CpMn(CO)_2(CS)$[7] and $[CpFe(CS)(CO)L]^+$.[11] On the other hand, when $k_{\rm CO}[M(CO)_{n+1}] > 17.1$ mdyn/Å, the π-acceptor to (σ + π)-donor ratio is lower for CS than for CO. This is in agreement with the infrared spectrum of $[CpMn(CS)(CO)(NO)]^+$ [9] and the ^{13}C NMR data for $[CpFe(CO)_2(CS)]^+$.[7] It presumably also applies to $[CpMn(CO)_2(CS)]^+$, the species actually involved in the mass spectral dissociation energy studies of $CpMn(CO)_2(CS)$.[3] Finally, the integrated infrared intensities for $CpMn(CO)_2(CS)$[8] and Mössbauer spectra of $[CpFe(CO)_2(CS)]^+$ [10] have been used to show that on an absolute basis CS is a better π acceptor than CO. Combined with the lower π-acceptor to (σ + π)-donor ratio found for CS in $[CpFe(CO)_2(CS)]^+$, this implies that for this compound CS is also a better donor than CO on an absolute scale. Thus, a unified understanding of the relative ligating properties of CS and CO is possible but only when all of the experimental evidence is combined to provide a broader perspective on thiocarbonyl bonding interactions.

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(13) Several points should be noted here. (1) Most of the CO force constants in Table I can be derived with only the minimal assumptions of neglect of anharmonicity and energy factoring of the CO stretching modes. (Force constants for compounds **3b**, **8b**, **15b**, **17b**, **23b**, **25b**, and **26b** were not calculated because additional assumptions regarding spectral assignments and interaction force constants would be required.) (2) The assumption of CO energy factoring could break down if the CO and CS stretches were significantly coupled. Normal-coordinate calculations, however, indicate that the coupling is small,[6c] and its inclusion in a force constant refinement had little effect on $k_{\rm CO}$.[14] (3) The reported spectra were obtained in a variety of solvents. Examination of compounds for which more than one spectra have been reported (indicated by average $k_{\rm CO}$ values in Table I) suggest that the errors in $k_{\rm CO}$ are probably about 0.1–0.2 mdyn/Å.
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Department of Chemistry[21]
University of California
Los Angeles, California 90024

Mark A. Andrews

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One-Electron Mechanism for the Electrochemical Reduction of Molecular Oxygen

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Sir:

There is major interest in the electrochemical reduction of molecular oxygen in aqueous solutions. In part this is due to its relevance to the development of hydrogen–oxygen fuel cells and metal–air batteries. Oxygen is a readily available and convenient oxidizing agent which theoretically is capable of undergoing a four-electron reduction to water at a standard potential of +0.98 V vs. the saturated calomel electrode. Several comprehensive reviews on the reduction of oxygen in aqueous solutions have appeared during the last decade.[1–4]

Evidence for the one-electron reduction of oxygen in aprotic solvents was first presented in 1965–1967[5–8] and has resulted in numerous additional investigations.[9] These have led to the confirmation that superoxide ion is the reduction product in aprotic media and is generated in aqueous media[10–12]

On the basis of previous studies of the electrochemical reduction of oxygen in both aqueous[13–15] and aprotic[6,16,17] media, together with the consideration of the entire body of experimental data for oxygen reduction,[1–4] two mechanistic schemes are proposed for the reduction process. One is based on an initial one-electron reduction of oxygen to superoxide ion, followed by chemical reactions which involve superoxide ion and are governed by solution conditions. It is common to both aqueous and aprotic media. The other applies to noninert electrodes in aqueous media and involves a preceding chemical reaction with the electrode instead of direct electron transfer to molecular oxygen. Direct electrochemical reduction of oxygen to water or hydroxide by a four-electron process does not occur.[18]

Reliable numerical values for the standard potential of the O_2/O_2^- couple[19,20] and for the rate constants for reactions of reactive oxygen species in solution[21] recently have become available. As a result, the oxygen-reduction schemes can be formalized in terms of pathways that (a) are consistent with experimental observations, (b) are thermodynamically and kinetically favored, and (c) are limited to a one-electron electrochemical process.

Scheme 1. The experimental observations clearly support the conclusion that the first step in the reduction of oxygen, in both aprotic and aqueous media, is the one-electron reduction to superoxide ion

$$O_2 + e^- \rightleftharpoons O_2^- \qquad (1)$$

for which the standard potential is –0.58 V[22] as determined in aqueous solution.

Reduction in aprotic media proceeds reversibly at potentials around –0.8 V and is independent of solvent and electrode material.[5–8] (The differences between the standard potential and the aprotic media potentials probably are due to solvation effects.) Long lifetimes are observed for superoxide ions in aprotic media, especially in solvents such as dimethyl sulfoxide and pyridine, which tenaciously hold onto residual protons. In the presence of protons or small cations, the potential becomes more positive and, in the case of protons, the reduction becomes a two-electron process that yields hydrogen peroxide.

An aqueous solution can be made to approximate an aprotic medium by making it strongly alkaline and providing it with a hydrophobic surfactant.[10–12] In such a solution, superoxide ion is formed and exhibits a significant lifetime.[10–12] The standard potential that is calculated from the data for the reduction process is –0.54 V,[10,11b,23] which is in good agreement with the currently accepted value of –0.58 V.[22] The formation of stable superoxide ion also is observed in the reduction of oxygen at a carbon paste electrode in alkaline media.[24] The reduction and reoxidation on carbon paste occurs at about –0.6 V; superoxide ion is not observed in nonalkaline solutions.

The direct reduction of superoxide ion cannot be a significant step in the overall reduction of oxygen to peroxide or water. Whereas the standard potential for the reaction

$$O_2^- + H_2O + e^- = HO_2^- + OH^- \qquad (2)$$

is –0.08 V,[19] the electrochemical reduction of superoxide ion occurs at a highly negative potential (in dimethyl sulfoxide it occurs at –2.0 V[6,16]). Obviously, the next step in the reduction of oxygen requires the interaction between superoxide ions and protons. We propose that this interaction and the subsequent chemical reactions are common to both aprotic and aqueous media.

In the presence of protons (or a proton source), superoxide ion participates in a series of reactions[21]

$$H^+ + O_2^- \rightleftharpoons HO_2 \quad pK_a = 4.88 \qquad (3)$$

$$2O_2^- + 2H_2O \rightarrow H_2O_2 + O_2 + 2OH^- \quad k_1 < 100\ M^{-1}\ s^{-1} \qquad (4)$$

$$O_2^- + HO_2 + H_2O \rightarrow H_2O_2 + O_2 + OH^- \quad k_2 = 8.5 \times 10^7 \qquad (5)$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \quad k_3 = 7.6 \times 10^5 \qquad (6)$$

The effect of protons on the electrochemical reduction of oxygen in aprotic media is dramatic; the reduction potential becomes more positive and the one-electron process gives way to an apparent irreversible two-electron process.[5–8] This behavior and the spontaneous reaction between superoxide ion and ammonium ion to form oxygen and hydrogen peroxide[6] are consistent with a reaction pathway that is represented by equations 3 and 5 and/or 6.[25] The oxygen formed in the disproportionation of superoxide undergoes reduction by the same pathway. The net reaction is

$$O_2 + 2H^+ + 2e^- = H_2O_2 \quad E^\circ = +0.43\ V^{26} \qquad (7)$$

This pathway accounts for the positive shift of the reduction potential, the production of hydrogen peroxide, and the apparent two-electron stoichiometry; it also avoids reduction processes that require more than a single electron (such as eq 7) or unstable reactant species, e.g.

$$HO_2 + H^+ + e^- = H_2O_2 \quad E^\circ = +1.17\ V \qquad (8)$$

even though they are energetically favored.

There is little doubt that superoxide ions react with protons and cause the shift of the reduction potential to more positive values. Further substantiation is provided by similar effects that are observed in the presence of metal cations which form stable superoxide products.[8,27,28] The combined information obtained in several solvents indicates that the shift in potential is due solely to complexation or precipitation of superoxide ion. There is no increase in the electron-per-oxygen molecule mole ratio except when catalytic disproportionation of superoxide occurs.

The proposal of a common one-electron reduction mechanism for molecular oxygen is supported convincingly by the data for the polarographic reduction of oxygen in dimethyl sulfoxide–water mixtures.[29] Up to a water content of about 8 vol %, the reduction of oxygen is a one-electron process which exhibits ac polarographic reversibility. Above 10% water content, the electron-per-oxygen molecule mole ratio rapidly increases with increasing water content to a maximum value of 2 at about 35% water. A concomitant shift of the reduction potential to more positive values occurs and levels off at the pH-independent value observed in aqueous media.

Reduction of oxygen at inert electrodes in aqueous solutions is first order in oxygen and independent of pH (approximately pH 2–12).[1,13–15] The reduction potential also is independent of electrode material, i.e., is the same at mercury and at platinum. For these conditions there is extensive evidence[1,4,13,14] that the rate-determining step is the one-electron-transfer reduction of oxygen (eq 1). We believe that the disappearance of superoxide ion follows the identical path it does in aprotic media, i.e., protonation followed by disproportionation, and that it does not involve the electrochemical reduction of superoxide ion or the protonated species HO_2.

By invoking the same mechanism, we again can explain the formation of hydrogen peroxide at inert electrodes in aqueous media[1,13–15] and preclude electrochemical reduction steps that involve multielectron transfer or unstable reactants. We in fact take issue with any mechanism that requires the electrochemical reduction of superoxide species;[1,3] the lifetimes of the superoxides in the presence of protons or water are too short.

For aqueous conditions the effective rate constants for the disproportionation of superoxide can be estimated for different pH values.[21] At pH 2 the effective rate constant for eq 6 is $0.87 \times 10^6\ M^{-1}\ s^{-1}$, with the reduction sequence represented by eq 1, 3, and 6 to give an overall reduction represented by eq 7. The maximum effective rate constant of $21 \times 10^6\ M^{-1}\ s^{-1}$ is obtained at pH 4.88 (equivalent to the pK_a for eq 3). The reduction sequence is represented by eq 1, 3, and 5 again to give an overall process represented by eq 7. At pH 11, the effective rate constant is about $200\ M^{-1}\ s^{-1}$, with the reduction sequence represented by eq 1 and 4 to give an overall process represented by

$$O_2 + H_2O + 2e^- = HO_2^- + OH^- \quad E^\circ_B = -0.33\ V \qquad (9)$$

for which the standard potential at pH 11 is –0.24 V. At this pH, about 80% of the peroxide is present as H_2O_2.

Clearly, the superoxide disproportionation reactions are fast over a broad pH range, including moderately alkaline solutions. Between pH 2 and pH 13, for a wide variety of metal electrodes (including platinum, palladium, gold, silver, and nickel,[13] mercury,[30] and carbon[31]) oxygen is reduced at a potential near –0.2 V; for mercury electrodes at high pH (pH >11) the reduction becomes reversible.[32]

Scheme 2. The reduction of oxygen in aprotic solvents and on inert electrodes in aqueous media is explained by scheme

1. In contrast, the reduction of oxygen at freshly preoxidized electrodes is pH dependent, yields negligible amounts of hydrogen peroxide, and occurs at the same potential as that for the metal oxide of the electrode material.[13,14] The previously proposed mechanism[13,14] continues to provide a plausible explanation for these observations

$$\mathrm{M(OH)_2 + 2H^+ + 2e^- \rightarrow M + 2H_2O} \qquad (10a)$$

$$\mathrm{M(OH)_2 + 2e^- \rightarrow M + 2OH^-} \qquad (10b)$$

$$\mathrm{2M + O_2 + 2H_2O \rightarrow 2M(OH)_2} \qquad (11)$$

In this mechanism, fresh metal oxide, $M(OH)_2$, is electrochemically reduced and re-formed by oxygen in solution. The scheme satisfies the requirement that the reduction potential and rate of reaction be dependent on the electrode material, M, and pH. The net reaction is

$$\mathrm{O_2 + 2H_2O + 4e^- = 4OH^-} \quad E°_B = +0.15 \text{ V} \qquad (12)$$

or

$$\mathrm{O_2 + 4H^+ + 4e^- = 2H_2O} \quad E° = +0.98 \text{ V} \qquad (13)$$

and does not involve formation of peroxide. Representative experimental reduction potentials at platinum are +0.30 and −0.32 V at pH 2 and pH 13, respectively.[13] Although eq 10 clearly represents the rate-determining step in the reduction of oxygen on preoxidized electrodes, some oxygen may react directly at freshly reduced electrode sites (scheme 1) to form trace amounts of peroxide.

In summary, there is no experimental or mechanistic basis for two-electron or four-electron processes in the direct electrochemical reduction of molecular oxygen. On the basis of the body of experimental data in support of mechanistic scheme 1, the one-electron-transfer process for reduction of molecular oxygen is concluded to be reversible and independent of electrode materials and solution conditions. The belief that the electrode surface is catalytic for the electron-transfer process is unjustified and not supported by the experimental data. Hence, the search for electron-transfer catalysts for oxygen reduction is a futile enterprise; the effective potential is limited to −0.2 V. Prechemical atom-transfer catalysts (eq 10 and 11 of scheme 2) can yield higher potentials that correspond to the reduction of the metal oxide.

The proposition of a one-electron mechanism for the electron-transfer reduction of oxygen and the associated conclusions present significant ramifications relative to the development of improved fuel cells and metal–air batteries. To date the practical forms of such systems have used strongly acidic or basic electrolytes. Such solution conditions normally cause scheme 2 to be the dominant reduction process for molecular oxygen at metal electrodes. Hence, the search for effective catalytic materials should be in this context rather than in terms of a one-electron-transfer process.

Finally, the concept of a one-electron mechanism for the electrochemical reduction of molecular oxygen is compatible with the current understanding of the biological electron-transfer reduction of oxygen and in accord with the mechanistic importance of superoxide ion.[19-21]

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Department of Chemistry
University of California
Riverside, California 92502

Donald T. Sawyer*
Eddie T. Seo

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Mode of Bonding of Dinitrogen Oxide (Nitrous Oxide) in (Dinitrogen oxide)pentaammineruthenium

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Sir:

(Dinitrogen oxide)pentaammineruthenium, $[Ru(NH_3)_5N_2O]^{2+}$, is at present the only known complex containing coordinated N_2O. In order to characterize the properties of N_2O as a ligand molecule, it is important to establish the mode of bonding of N_2O. In earlier work[1,2] some evidence was presented which indicated that N_2O was bonded to the ruthenium via the terminal N atom (i.e., Ru–N–N–O). Recently Diamantis and Sparrow and collaborators[3,4] stated that force constant calculations show the N_2O to be bonded via the O atom (i.e., Ru–O–N–N). We wish to comment on their result, and on the bonding of N_2O in $[Ru(NH_3)_5N_2O]^{2+}$.

Examination of Table II of ref 3 shows a very large variation in some of the force constants as the negative ions are changed. Thus the Ru–N stretching constants for the Ru–N–N–O model and the Ru–O stretching constant for the Ru–O–N–N model change by more than a factor of 2 while the frequencies assigned to the Ru–N or Ru–O mode are in the range 300–340 cm^{-1}. The stretching constants for the central bond of each model also change over a comparable range. These improbably large variations prompted us to recalculate the frequencies using the force constants of Diamantis and Sparrow. The frequencies obtained[5] by us differed from the observed by as much as 300 cm^{-1}. We therefore suspected the vibrational