THE REDOX POTENTIAL OF THE SYSTEM OXYGEN–SUPEROXIDE

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1. Introduction

It is now clear that the superoxide radical (O_2^- generated in a large number of reactions of biochemical importance, in both enzymatic and non-enzymatic oxidations [1]. A reliable value for the O_2/O_2^- redox potential is needed in order that thermodynamic calculations and restrictions can be applied to reactions involving O_2^-. However, until recently all estimates of $E_0(O_2/O_2^-)$ which purported to have error limits less than about 0.1–0.2 V were based on indirect calculations as opposed to direct experimental data. Latimer's [2] calculated value was –0.56 V, while a later calculation by George [3] (as amended by Sutin [4]) gave –0.59 V. These values have been criticised as being too low to explain experimental data [5,6]. For example Yamazaki et al. inferred a potential of 0 to –0.3 V from their experiments on the autoxidation of ferroperoxidase [7], while in a slightly later paper [5] they suggested a value in the region of –0.3 V.

Recently three more precise values of $E_0(O_2/O_2^-)$ based directly on experimental data have been published. Chevalet et al. [8] found a value of –0.27 V from polarographic work, while Berdnikov and Zhuravleva [9] have derived a value of –0.33±0.01 V from the equilibrium constant for

$$H_2O_2 + Fe^{3+} \rightleftharpoons HO_2^- + H^+ + Fe^{2+}.$$

A very different value was published by Rao and Hayon [10], who deduced a potential of +0.15 V (their value at pH 7.0). In the present communication a fourth value, in good agreement with the first two, is derived from published data. It is also shown that the discrepancy between Rao and Hayon's value and the other three is attributable to errors in Rao and Hayon's calculation.

2. Results

The convention is adopted that $E_0(O_2/O_2^-)$ denotes the standard potential of the reaction $O_2 + e_{aq}^- \rightarrow O_2^-$ relative to a standard hydrogen electrode, and similarly for other redox couples. For reactions in which protons are involved, and hence the potential is dependent on pH, the symbol E_0' is used to specify pH 7.0, e.g. E_0' (O_2^-/H_2O_2) for $O_2^- + 2H^+ + e_{aq}^- \rightarrow H_2O_2$.

Patel and Willson [11] have measured the equilibrium constant for the reaction

$$O_2^- + \text{duroquinone (DQ)} \rightleftharpoons O_2 + \text{durosemiquinone } (DQ^-)$$

as $K_c = (2.3\pm0.2) \times 10^{-2}$ at pH 7.0. This can be used to derive a value for $E_0(O_2/O_2^-)$, once $E_0(DQ/DQ^-)$ is established. Consider the following equilibria, in which DQH_2, DQH^- and DQ^{2-} stand for the durohydroquinone neutral form, monoanion, and dianion respectively:

$$DQH_2 \rightleftharpoons DQH^- + H^+, K_1 = [DQH^-]\ [H^+]/[DQH_2] = 10^{-11.25} \text{ (ref. [12])}$$

$$DQH^- \rightleftharpoons DQ^{2-} + H^+, K_2 = [DQ^{2-}]\ [H^+]/[DQH^-] = 10^{-13.2} \text{ (ref. [13])}$$

$$DQ^{2-} + DQ \rightleftharpoons 2DQ^-, K_3 = [DQ^-]^2/[DQ^{2-}]\ [DQ]) = 1.3 \text{ (ref. [14])}.$$

These values for the equilibrium constants are as given in Bishop and Tong's list [13] for duroquinone and eleven other quinones. By addition:

$$DQ + DQH_2 \rightleftharpoons 2DQ^{\cdot -} + 2H^+, K = K_1K_2K_3,$$

and for the forward reaction at pH 7, $\Delta G^{0\prime} = -RT\ln(K_1K_2K_3 \cdot 10^{14})$. Furthermore, for

$$DQ + 2H^+ + 2e^-_{aq} \rightarrow DQH_2, \Delta G^{0\prime} = -2E_0^{\prime}(DQ/DQH_2) \cdot F,$$

and $E_0^{\prime}(DQ/DQH_2) = +0.05$ V (ref. [15]). Combining these equations, it follows that for

$$DQ + e^-_{aq} \rightarrow DQ^{\cdot -},$$

$E_0(DQ/DQ^{\cdot -}) = -0.25$ V, and also $E_0^{\prime}(DQ^{\cdot -}/DQH_2) = +0.35$ V. (Yamazaki et al. [5] give similar data for ascorbate and hydroquinone, the latter in good agreement with values calculated from Bishop and Tong [13]). Since the pK of durosemiquinone is 5.1 (ref. [16]) inclusion of the equilibrium $DQ^{\cdot -} + H^+ \rightleftharpoons DQH\cdot$ makes little difference. This value for $E_0(DQ/DQ^{\cdot -})$ when combined with Patel and Willson's equilibrium constant and converted to the thermodynamic standard state of oxygen yields

$$E_0(O_2/O_2^{\cdot -}) = -0.33 \text{ V, at } p_{O_2} = 1 \text{ atm}, [O_2^{\cdot -}] = 1 \text{ M},$$

given $\Delta G^0(O_{2\,aq}) = +3.95$ kcal mol^{-1} (ref. [3]).

Rao and Hayon [10] obtained their value for $E_0(O_2/O_2^{\cdot -})$ by studying equilibria of the type

$$O_2^{\cdot -} + Q \rightleftharpoons Q^{\cdot -} + O_2$$

for various quinones, at ~ 100 μsec after pulse radiolysis of the solution. The ratio $[Q^{\cdot -}]/[O_2^{\cdot -}]$ varied in a regular way with the two-electron potential $E_0^{\prime}(Q/QH_2)$ and was unity at $E_0^{\prime}(Q/QH_2) = +0.15$ V. They equated this with $E_0(O_2/O_2^{\cdot -})$. In the first place, their result refers to $[O_2] = 1$ M, and correction to $p_{O_2} = 1$ atm changes the potential by −0.17V. Secondly, Rao and Hayon worked at $[O_2]/[Q] = 26$, and correction for this is equivalent to a change of −0.08 V. Their figures then become in good agreement with those of Patel and Willson [11], who made similar measurements. The more serious error in Rao and Hayon's reasoning lay in equating $E_0^{\prime}(Q/QH_2)$ with $E_0(Q/Q^{\cdot -})$. Consider Rao and Hayon's data for 2,5-dimethylquinone ($E_0^{\prime}(Q/QH_2) = +0.18$ V; ref. [15]). At $[O_2]/[Q] = 26$ they found 61% electron transfer, or $[Q^{\cdot -}]/[O_2^{\cdot -}] = 1.56$. This implies an equilibrium constant $K_c = 41$. For 2,5-dimethylquinone, Bishop and Tong's data [13] lead to

$$E_0(Q/Q^{\cdot -}) = E_0^{\prime}(Q/QH_2) - 0.24 \text{ V}.$$

Applying these corrections one finds $E_0(O_2/O_2^{\cdot -}) = -0.33$ V (at $p_{O_2} = 1$ atm), in agreement with the other values.

3. Discussion

The four values for $E_0(O_2/O_2^{\cdot -})$ are listed together in table 1. Although it is difficult to explain the disagreement between Chevalet et al. and the others, the excellent agreement of the last three values suggests that $E_0(O_2/O_2^{\cdot -}) = -0.33 \pm 0.01$ V can now be generally accepted.

Table 1
Values of $E_0(O_2/O_2^-)$ based on experimental measurements

E_0, V	Reference
−0.270	Chevalet et al. [8]
−0.33±0.01	Berdnikov and Zhuravleva [9]
−0.33	Calculated from Patel and Willson [11] and Bishop and Tong [13]
−0.33	Rao and Hayon [10], corrected

The superoxide ion can also act as an oxidising agent:

$$O_2^{\cdot -} + 2H^+ + e^-_{aq} \rightarrow H_2O_2,$$

for which

$$E_0^{\prime}(O_2^{\cdot -}/H_2O_2) = 2E_0^{\prime}(O_2/H_2O_2) - E_0(O_2/O_2^{\cdot -}).$$

Lewis and Randall [17] calculated $E_0^{\prime}(O_2/H_2O_2) = +0.27$ V, and a later calculation [18] increased this to +0.295 V. It is however preferable to use the value from experimental measurements. The average of four such measurements [19–22], three at alkaline pH and one at pH 0, leads to $E_0'(O_2/H_2O_2) = +0.305 \pm 0.005$ V, after including a pK at 11.65 (ref. [23]) for the reaction $H_2O_2 \rightleftharpoons HO_2^- + H^+$ in the conversion of alkaline data to pH 7. With $E_0(O_2/O_2^-)$ taken as -0.33 ± 0.01 V, it then follows that

$$E_0'(O_2^-/H_2O_2) = +0.94 \pm 0.02 \text{ V}.$$

Chevalet et al. [8] give a complete potential – pH diagram for the oxidation states $O_2^0 - O_2^{-I} - O_2^{-II}$, from pH −1 to pH +18. At high pH values the system $O_2^0 - O_2^{-I}$ has a potential equalling that calculated, $E_0(O_2/O_2^-)$, independent of pH. As the pH is lowered the potential starts to rise when the pK for $H^+ + O_2^- \rightleftharpoons HO_2^\cdot$ is approached (pK = 4.45, ref. [24]), and continues to rise at lower pH; there is a second pK at pH ~1.2.

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