Reduction Potentials of One-Electron Couples Involving Free Radicals in Aqueous Solution

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Reduction of an electron acceptor (oxidant), A, or oxidation of an electron donor (reductant), A^{2-}, is often achieved stepwise *via* one-electron processes involving the couples $A/A^{\cdot -}$ or $A^{\cdot -}/A^{2-}$ (or corresponding prototropic conjugates such as $A/AH^{\cdot}$ or $AH^{\cdot}/AH_2$). The intermediate $A^{\cdot -}(AH^{\cdot})$ is a free radical. The reduction potentials of such one-electron couples are of value in predicting the direction or feasibility, and in some instances the rate constants, of many free-radical reactions. Electrochemical methods have limited applicability in measuring these properties of frequently unstable species, but fast, kinetic spectrophotometry (especially pulse radiolysis) has widespread application in this area. Tables of *ca.* 1200 values of reduction potentials of *ca.* 700 one-electron couples in aqueous solution are presented. The majority of organic oxidants listed are quinones, nitroaryl and bipyridinium compounds. Reductants include phenols, aromatic amines, indoles and pyrimidines, thiols and phenothiazines. Inorganic couples largely involve compounds of oxygen, sulfur, nitrogen and the halogens. Proteins, enzymes and metals and their complexes are excluded.

Key words: aqueous solution; data compilation; electron transfer; equilibria; equilibrium constants; free radical; oxidation potential; radical; radiolysis; reduction potential; redox potential; review.

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1. Introduction

Many reactions of free radicals involve one-electron transfer. If an electron acceptor, A is reduced to a radical, A·⁻ then the possibility of further or competing reactions involving other electron acceptors, B, C etc.:

1 $$A\cdot^- + B \rightleftharpoons A + B\cdot^-$$

2 $$A\cdot^- + C \rightleftharpoons A + C\cdot^-$$

3 $$B\cdot^- + C \rightleftharpoons B + C\cdot^-$$

can be calculated if the one-electron reduction potentials $E°(A/A\cdot^-)$, $E°(B/B\cdot^-)$ etc. are known. Thus the equilibrium constant, K_1 for reaction *1* is related to the difference ΔE_1 between the couples:

$$\Delta E_1^\circ = E°(B/B\cdot^-) - E°(A/A\cdot^-) \qquad (1)$$

by the expression

$$\Delta G_1^\circ = -nF\Delta E_1^\circ = -RT\ln K_1 \qquad (2)$$

where K_1 is the ratio of activities

$$K_1 = \frac{(a_A a_{B^-\cdot})}{(a_B a_{A^-\cdot})}\,. \qquad (3)$$

Except at high ionic strengths (see below, Sec. 3.8) we can replace activities by concentration so that

$$K_1 \approx \left(\frac{[A][B\cdot^-]}{[B][A\cdot^-]}\right)\,. \qquad (4)$$

At 298 K from Eq. (2) we have

$$\Delta E_1^\circ/\text{mV} \approx 59.1 \log K_1 \qquad (5)$$

and differences of ca. 60 mV in reduction potential correspond to an order of magnitude change in equilibrium constant.

Even when reactions are irreversible and equilibria are not achieved, there are many instances where the rate constants for the reaction are reflected in the reduction potentials of electron donor or acceptor (see below, Sec. 7.2). Current interest in reactions of excited states with electron donors or acceptors, often involving electron transfer, is aided by the relative ease by which reduction potentials of many substances can be measured electrochemically in the aprotic solvents often used in such experiments. In water, however, free radicals are often too short-lived for conventional electrochemical methods to be used. The ability to observe directly the lifetimes and reactions of unstable intermediates using kinetic spectrophotometry offers obvious advantages. Detailed descriptions of electrochemical techniques can be readily found in the literature, and this introduction therefore concentrates on the more recent application of fast, kinetic methods to derive electrochemical potentials. As outlined below, pulse radiolysis and flash photolysis techniques can be used to measure equilibrium constants of redox reactions before transient species can decay. Neta[1] has summarized some early studies of redox properties of free radicals using the pulse radiolysis technique.

Dorfman and colleagues[2] used pulse radiolysis to observe electron-transfer equilibria of arene radicals in ethanol, and Patel and Willson[3] measured equilibrium constants for electron transfer between semiquinones and oxygen in water. The latter data and approach enabled Wood,[4] Ilan et al.[5] and Meisel and Czapski[6] to obtain the definitive value of the important couple $E°(O_2/O_2\cdot^-)$. Meisel and Neta[7] extended the method to include reversible electron transfer between quinones and nitroaromatic compounds, and Steenken and Neta[8] measured equilibria between phenoxyl radicals and hydroquinones or phenoxides at high pH. As a result of these pioneering studies, there are now many reliable values of thermodynamically-reversible one-electron reduction potentials of couples involving unstable free radicals in aqueous solution.

2. Reduction Potentials of Couples Involving Unstable Species

2.1. Stepwise Addition of Electrons

Many reactions formally involving two-electron couples A/A^{2-} are known to proceed in two one-electron steps, $A/A\cdot^-$ and $A\cdot^-/A^{2-}$. (*For simplicity we presently ignore protonation here*, but recognize that e.g. $A\cdot^-$ or A^{2-} may exist as conjugate acids at the pH of interest.)

The intermediate $A\cdot^-$, generally a free radical in most of the cases tabulated here, may be produced *either* by reduction of A *or* by oxidation of A^{2-} (see below, Sec. 3.1, 3.2). The two-electron potential, $E°(A/A^{2-})$ is related to the one-electron couples by

$$2E°(A/A^{2-}) = E°(A/A\cdot^-) + E°(A\cdot^-/A^{2-}). \quad (6)$$

Various alternative symbols are used for reduction potential, e.g. we can recognise the first- and second- one-electron potentials by denoting $E(A/A\cdot^-)$ as E^1 and $E(A\cdot^-/A^{2-})$ as E^2 with subscripts for pH, e.g. E^1_7, $E^2_{13.5}$. The standard reduction potential is usually denoted by $E°$. The distinction between standard potentials and measured quantities is not always clear, and is a particular problem where either ground state or radical species are protonated or dissociate in prototropic equilibria. A discussion of this point and recommendations for symbolism and description of reduction potentials is postponed to Sec. 4 when prototropic equilibria will have been considered in more detail.

2.2. Standard States, Reference Potentials and Sign Conventions[9-11]

The standard states of unit activity (approximately 1 mol dm^{-3} concentration) for solids and liquids and unit fugacity (approximately 1 atmosphere partial pressure) for gases are used. *The latter convention frequently leads to errors in calculation*, particularly in reactions involving the important $O_2/O_2\cdot^-$ couple. Thus the standard potential is $E°(O_2/O_2\cdot^-) \approx -325$ mV whereas the potential of the couple $E(O_2(1 \text{ mol dm}^{-3})/O_2\cdot^-) \approx -155$ mV.[4-6] The difference can be appreciated by application of the Nernst equation (see Sec. 4.2, eq. (14), below) with the oxygen concentration of ~1.3 mmol dm^{-3}. The standard state pressure was defined as 101.325 kPa; changing to a new standard state of 100 kPa = 1 bar alters potentials by only 0.17 mV, negligible in the present context. The convention of the standard state of pure elements being the normal physical state existing at 1 atmosphere and 298 K introduces another complication; thus the standard potential $E°(I_2/I_2\cdot^-)$ refers to solid elemental iodine and not ~ 1 mol dm^{-3} in aqueous solution.

The reference potential throughout these tables is the normal or standard hydrogen electrode (s.h.e.). Many electrochemical measurements are originally referred to the saturated calomel electrode (s.c.e.); these have been converted to s.h.e. by adding 244 mV if the measurements were at ~ 298 K (241 mV at 303 K). A few measurements originally referred to the calomel electrode at 1 mol dm^{-3} KCl (normal), n.c.e.; the correction in this case is 280 mV. The Ag/AgCl electrode is 222 mV lower than s.h.e. at 298 K.

The IUPAC convention of writing couples as *reduction* potentials is followed exclusively. Thus for the reduction of A to $A\cdot^-$ the couple is $E(A/A\cdot^-)$; an obsolete convention of describing couples as *oxidation* potentials is to be discouraged. Even though the conversion of A^{2-} to $A\cdot^-$ involves oxidation, it is preferable to write all couples as reduction potentials: the ease of oxidation of A^{2-} to $A\cdot^-$ is characterized as the reduction potential of the radical $A\cdot^-$, i.e. $E(A\cdot^-/A^{2-})$. The standard use of the term 'reduction potential', exclusion of the obsolete 'oxidation potential' and avoidance of the ambiguous 'redox potential' serves not only to clarify the definition of the couples but also aids information retrieval in computer systems. Further discussion of the definitions, and use of symbols for reduction potentials is postponed until Sec. 4 (below), when their application should be more apparent.

2.3. Ease of Reduction and Ease of Oxidation

With these conventions, substances A with more positive reduction potentials for the couple $A/A\cdot^-$ are more powerful oxidants (A easier to reduce). Substances A^{2-} with more negative reduction potentials for the couple $A\cdot^-/A^{2-}$ are more powerful reductants (oxidation of A^{2-} more favorable). Thus 1,4-benzoquinone (Q) with $E°(Q/Q\cdot^-) = 78$ mV is a more powerful oxidant than its 2,3,5,6-tetramethyl derivative, duroquinone (DQ) with $E°(DQ/DQ\cdot^-) = -244$ mV. The semiquinone $DQ\cdot^-$ of duroquinone will tend to be oxidized by benzoquinone, forming benzosemiquinone, depending on the relative concentrations of the reactants as described by equilibrium *1*. These differences can be readily understood because of the electron-donating influence of the methyl groups. Phenols, such as 1,4-dihydroxybenzene (hydroquinone) are fully dissociated to phenoxide ions, PhO^- at high pH (highest pK_a in this case ~ 11.4). Reduction potentials at pH ~ 13.5 for the phenoxyl radical/phenoxide couple, $E(PhO\cdot/PhO^-)$ of ~ 23 and 700 mV have been calculated or measured for hydroquinone and phenol, respectively. Hence hydroquinone is much more easily oxidized than phenol. The phenoxyl radical obtained upon one-electron oxidation of phenol is thermodynamically capable of oxidizing hydroquinone unless there is a hugely unrealistic excess of phenol to hydroquinone to modify the position of the electron-transfer equilibrium. The phenoxyl radical derived from phenol is a more powerful oxidant than that derived from hydroquinone; the *reduction* potential of the former radical is more positive than that from the latter.

3. Observation of One-Electron Transfer Equilibria

3.1. Generating the Couple $A/A\cdot^-$ by Reducing Radicals From Water Radiolysis[12-15]

The radiolysis of water produces e^-_{aq}, H· and ·OH radicals. The hydrated electron, e^-_{aq}, will generally reduce A to $A\cdot^-$, often in a diffusion-controlled reaction. The hydroxyl radical, $\cdot OH$, is oxidizing and can be prevented from reacting with A:

4 $$\cdot OH + A \rightarrow \text{products}$$

by several methods:

a. *tert*-Butyl alcohol is added, which reacts with $\cdot OH$ to yield a radical which is of only moderate reactivity and *may* not react with A or other solutes on the timescale of interest:

5 $$\cdot OH + (CH_3)_3COH \rightarrow H_2O + (\dot{C}H_2)C(CH_3)_2OH.$$

Not infrequently, however, $A\cdot^-$ does react with the alcohol radical from reaction *5*. Loss of $A\cdot^-$ via this unwanted route can be avoided by alternatives b and c (below) or by using minimal dose (radical concentration).

b. 2-Propanol is added which reacts with $\cdot OH$ to yield *predominantly* an α-hydroxyalkyl radical which will *usually* produce the desired species $A\cdot^-$ by electron-transfer:

6 $$\cdot OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2\dot{C}OH$$

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

The fraction of $\cdot OH$ attack on $-CH_3$ to yield a β-hydroxyalkyl radical, with similar properties to that produced in reaction *5* is $\sim 15\%$.[16] Hence a fraction of $A\cdot^-$ may be lost via this unwanted reaction, albeit on a timescale often too slow to interfere with electron-transfer equilibration (see below, Sec. 3.5).

c. The $\cdot OH$ scavenger of choice when the longest 'natural' lifetime of $A\cdot^-$ is sought is formate (usually the sodium salt). The $CO_2\cdot^-$ radical formed upon scavenging $\cdot OH$ with HCO_2^-:

8 $$\cdot OH + HCO_2^- \rightarrow H_2O + CO_2\cdot^-$$

will *generally* produce the same species $A\cdot^-$ produced by reduction with e_{aq}^-:

9 $$CO_2\cdot^- + A \rightarrow CO_2 + A\cdot^-$$

10 $$e_{aq}^- + A \rightarrow A\cdot^-$$

although a high ionic strength usually results (see below, Sec. 3.8).

One aims to have the rate of reactions *5*, *6* or *8* much greater than the rate of reaction *4*. Rate constants for reaction of $\cdot OH$ with many substances are known[17] or can be estimated with sufficient accuracy for this inequality to be satisfied. Usually the $\cdot OH$ scavenger will be used at concentrations of 0.1-0.2 mol dm^{-3}. Hydrogen atoms comprise ca. 10% of the total radicals and a fraction may react with e.g. $(CH_3)_2CHOH$ or HCO_2^- (*tert*-butyl alcohol is less reactive) depending on the solute reactivity. It cannot be assumed that $H\cdot$ will react with A to yield $A\cdot^-$. Especially with oxidants A of very low electron affinity it may not be safe to assume that reactions *7* and even *9* will yield $A\cdot^-$ and alternative (a) may be preferred in spite of the disadvantages noted.

3.2. Generating the Couple $A\cdot^-/A^{2-}$ by Oxidizing Radicals From Water Radiolysis[12-15]

Removing the reducing radical e_{aq}^- is simple:

11 $$e_{aq}^- + N_2O + H^+ \rightarrow N_2 + \cdot OH$$

and saturation with N_2O ($[N_2O] \approx 25$ mmol dm^{-3}) will prevent effectively the now unwanted reaction *10* if $k_{11}[N_2O] \gg k_{10}[A]$. Numerous values for k_{10} are tabulated.[17] The $H\cdot$ atoms are usually ignored but could be a source of error if the product(s) of $H\cdot + A^{2-}$ absorb significantly compared to $A\cdot^-$.

With A^{2-} = phenoxide ion, reaction *13* rapidly follows reaction *12* to yield the desired phenoxyl radical $A\cdot^-$ in basic solution:

12 $$\cdot OH + C_6H_5O^- \rightarrow HOC_6H_5O\cdot^-$$

13 $$HOC_6H_5O\cdot^- \rightarrow C_6H_5O\cdot + OH^-.$$

However, the lack of selectivity in reactions of $\cdot OH$ has led to the practice of converting it to a more selective oxidizing radical, e.g. $\dot{C}H_2CHO$:[18]

14 $$\cdot OH + HOCH_2CH_2OH \rightarrow HOCH_2\dot{C}HOH + H_2O$$

15 $$HOCH_2\dot{C}HOH \rightarrow \dot{C}H_2CHO + H_2O$$

16 $$\dot{C}H_2CHO + A^{2-} + H^+ \rightarrow A\cdot^- + CH_3CHO.$$

Alternative oxidizing systems more selective than $\cdot OH$ are the halogen or pseudohalogen radicals $X_2\cdot^-$ (X = halogen or thiocyanate etc.) and $N_3\cdot$:

17 $$\cdot OH + 2\,X^- \rightarrow OH^- + X_2\cdot^-$$

18 $$\cdot OH + N_3^- \rightarrow OH^- + N_3\cdot.$$

Rate constants of many one-electron oxidation reactions of these species have been tabulated:[19]

19 $$X_2\cdot^- + A^{2-} \rightarrow 2\,X^- + A\cdot^-$$

20 $N_3\cdot + A^{2-} \rightarrow N_3^- + A\cdot^-.$

Another useful system involves $SO_4\cdot^-$ (via $e_{aq}^- + S_2O_8^{2-}$)[19]

21 $SO_4\cdot^- + A^{2-} \rightarrow SO_4^{2-} + A\cdot^-.$

Since $k_4 \approx k_{14} \approx k_{17} \approx k_{18}$ we use [glycol], $[X^-]$, $[N_3^-]$ etc. $\gg$ [A], e.g. 1 mol dm^{-3} glycol or 0.1 mol dm^{-3} Br^-.

3.3. Generating Radicals by Flash Photolysis

The triplet state A* (e.g. of nitroaromatic compounds)[20,21] may be quenched by electron donors, D to yield radical-anions:

22 $A + h\nu \rightarrow A^*$

23 $A^* + D \rightarrow A\cdot^- + D\cdot^+$

although little application of this method to measuring reduction potentials has been reported.[20]

3.4. Electrochemical Measurements of Reduction Potentials in Aqueous Solution

Clark's classical text[22] includes methods by which one-electron potentials may be derived from electrochemical measurements, and Bard[23] has described general electrochemical methods. Some electrochemical methods require the intermediate $A\cdot^-$ to be relatively stable; this condition is easily met for A = bipyridinium dications[22] (viologens), some quinones at high pH[24], etc., and for A^{2-} = some phenylenediamines, and phenothiazines in acidic solution. Polarography with a time resolution compatible with pulse radiolysis[25] offers obvious advantages over conventional methods, but protonation of radicals is frequently accompanied by irreversibility of the reduction process. More recently, cyclic voltammetry has had some success[26-29] in determining reduction potentials involving both inorganic and organic radicals in aqueous solution; in this case, the theoretical treatment requires rapid loss of the radical[26,30,31].

3.5. Establishing a Redox Equilibrium: Kinetic Constraints

Many of the radiolytic reactions useful for generating radicals $A\cdot^-$ (*7,9,10,16,19-21*) are so rapid that at practical concentrations of A of the order 10 μmol dm^{-3} - 10 mmol dm^{-3}, the production of radicals $A\cdot^-$ and/or $B\cdot^-$ for the desired equilibrium *1* is complete a few microseconds after a radiation pulse. The rate of approach to equilibrium *1* is then controlled by k_1 and k_{-1}:

$$k_{1,\text{obs}} \approx k_1[B] + k_{-1}[A]. \tag{7}$$

This approximation is usually valid if pulse radiolysis or flash photolysis involves generation of ca. 1 - 10 μmol dm^{-3} $A\cdot^-$ and/or $B\cdot^-$ and $[A\cdot^-]$, $[B\cdot^-] \ll [A]$, [B]. Here $k_{1,\text{obs}}$ is the first-order rate constant (units s^{-1}) obtained by plotting the appropriate function of absorbance vs. time. As equilibrium *1* is approached, significant loss of $A\cdot^-$, $B\cdot^-$ (e.g. by disproportionation):

24 $2\,A\cdot^- \rightarrow A + A^{2-}$

must be negligible if K_1 is to be estimated reliably. While k_1 and/or k_{-1} may be of the order of 10^8 dm^3 mol^{-1} s^{-1} for many electron-transfer reactions, it is frequently observed that protonation of A, $A\cdot^-$, or A^{2-} slows down electron-transfer rate constants by orders of magnitude, and then equilibrium *1* may not be achieved in competition with reaction *24* etc. Thus deprotonation of hydroquinones, phenols, ascorbate etc. is often necessary to observe reversible electron-transfer reactions of these substrates.[8]

3.6. Calculation of Reduction Potentials From Concentrations at Equilibrium

By making the assumption that as [A], [B] is varied the radiolytic yield ($[A\cdot^-] + [B\cdot^-]$) remains constant, then[7]

$$K_1 \approx \frac{(A_{\text{obs}} - A_{A\cdot^-})}{(A_{B\cdot^-} - A_{\text{obs}})} \cdot \frac{[A]}{[B]}. \tag{8}$$

A_{obs} is the absorbance at a constant dose (constant total radical concentration) in the solution containing A and B, and $A_{A\cdot^-}$, $A_{B\cdot^-}$ are the absorbances at the selected wavelength of $A\cdot^-$ and $B\cdot^-$ alone. Alternative algebraic routes to K_1 have been used.[3,6] Under some circumstances a significant fraction of A, B may be converted to $A\cdot^-$, $B\cdot^-$ and calculation by an iterative procedure for the concentrations of A, B at equilibrium may be necessary.

3.7. Calculation of Reduction Potential From the Kinetics of the Approach to Equilibrium

From Eq. (7) we have:

$$\frac{k_{1,\text{obs}}}{[B]} \approx k_1 + k_{-1}\frac{[A]}{[B]}. \tag{9}$$

A plot of $k_{1,\text{obs}}/[B]$ vs. [A]/[B] yields an estimate of K_1 from the ratio (intercept/slope). Again, the kinetics must reflect only the approach to equilibrium *1* and there must be insignificant loss of $A\cdot^-$, $B\cdot^-$ by other routes.

3.8. Effects of Ionic Strength, Temperature and Solvent

If *either* both reactants *or* both products of reaction *1* are charged then K_1 defined by Eq. (4) will vary with ionic strength, *I*. We can either plot several measured values of ΔE_1 against (say) $I^{\frac{1}{2}}$ to extrapolate to zero ionic strength or use the Debye-Hückel equation to calculate activity coefficient ratios.[32] The limitations of such treatments to ionic strengths much lower than those used in many radiolysis experiments are well known. An alternative approach uses the Debye-Hückel-Brønsted-Davies expression for the primary kinetic salt effect:[33]

$$\log k = \log k^0 + 2z_A z_B A(I^{\frac{1}{2}}(1 + I^{\frac{1}{2}})^{-1} - BI) \qquad (10)$$

where the constants A, B vary with solvent and ions but are close to 0.5 and 0.2 respectively for water and typical ions. If for simplicity we abbreviate z_A, z_B to a,b (the charges on A,B) then reaction *1* may be written:

$$1' \qquad \mathrm{A}\cdot^{(a-1)} + \mathrm{B}^b \rightleftharpoons \mathrm{A}^a + \mathrm{B}\cdot^{(b-1)}.$$

It is readily shown that

$$\Delta E_0 = \Delta E_I + \Delta E_{\mathrm{corr}} \qquad (11)$$

where the correction term to be added to the value ΔE_I measured at an ionic strength I is:

$$\Delta E_{corr}/\mathrm{mV} \approx 59.1(b - a)f(I). \qquad (12)$$

The function $f(I)$ appropriate for many reactions in water at 298 K can be approximated to:

$$f(I) \approx 1.02(I^{\frac{1}{2}}(1 + I^{\frac{1}{2}})^{-1} - 0.2I). \qquad (13)$$

If e.g. A = a bipyridinium dication and B = a quinone sulfonate monoanion then $(b - a) = -3$ and $\Delta E_{corr} \approx -16$ and -49 mV at $I = 0.01$ and 0.2 respectively. At a given pH we may see $\mathrm{A}\cdot^-$ protonated but A not and the salt effect then requires more careful consideration; with complex molecules the effective charge may differ from the nominal net charge,[34] and experiments at several ionic strengths are desirable. Some other effects of ionic strength are considered in Sec. 5.

Little work has been done on the effects of temperature and solvent. The author has used data[35] for the temperature-variation of the reduction potential of 1,1'-dimethyl-4,4'-bipyridinium dication and its benzyl analogue to show that $E(\mathrm{A/A}\cdot^-)$ for A = the 2-nitroimidazole, misonidazole varies with temperature at pH 7 in aqueous solution with $\mathrm{d}E/\mathrm{d}T \approx -1.1$ to -1.8 mV K^{-1} depending on the viologen data used (unpublished work). Solvent effects (mixed aqueous: organic solutions) will vary widely, depending especially upon the net charges involved; illustrations of these effects have been presented.[36,37] Entropy changes can, of course, be estimated from $\mathrm{d}E/\mathrm{d}T$. Typical values of $\mathrm{d}E/\mathrm{d}T$ for viologen reference compounds are -0.4 to -0.9 mV K^{-1},[35] and for simple nitroaryl compounds are -1 to -2 mV K^{-1}. Thus the common practice of ignoring variations in experimental temperatures may introduce systematic errors in estimates of E° of several mV, aside from other uncertainties noted below.

3.9. Relative and Absolute Uncertainties Associated With Measurements

From Eq. (5) an uncertainty of ± 10% in K_I corresponds to ca. ± 2.6 mV in ΔE°_1. The lack of, or uncertainties in ionic strength corrections (where needed) may be *at least* of this order and in general values of ΔE°_1 are unlikely to be more accurate than ± 5 mV. The potentials of most redox indicators (see below, Sec. 5,6) are certainly not known to better than ± 5-10 mV and a realistic uncertainty in $E^\circ(\mathrm{A/A}\cdot^-)$ of ± 10 mV is probably the *minimum* associated with the data given in Tables 1-4. For couples of the form $\mathrm{A}\cdot^-/\mathrm{A}^{2-}$ (Tables 5-8) ΔE°_1 may often be measurable to ± 10 mV or so[8] but ionic strength effects, where present (either $a \neq 0$, $b \neq 0$ or $a \neq b$) in e.g. 0.5 mol dm^{-3} KOH may lead to treble this uncertainty in values of reduction potentials.

The potentials in the Tables are presented in integer millivolts mainly to minimize rounding errors where several values may be coupled together to facilitate calculations, or to facilitate calculation of equilibrium constants from which the potentials were derived. The *absolute* values of the potentials are seldom reliable to better than ± 10 mV, and many may be uncertain by ± 20 mV.

Couples involving protons (see below) introduce further uncertainties since thermodynamic pK_a's are frequently unavailable. The effects of these possible systematic errors are discussed further below.

4. Effects of Prototropic Equilibria Upon Reduction Potentials

4.1. Introduction

Reduction potentials refer to reactions of the form:

$$25 \qquad \text{oxidant} + n\mathrm{e}^- \rightarrow \text{reductant}.$$

The couples $\mathrm{A/A}^{2-}$, $\mathrm{A/A}\cdot^-$ and $\mathrm{A}\cdot^-/\mathrm{A}^{2-}$ may represent the reactions involved in the two-electron reduction of A to A^{2-}, or the two individual one-electron steps, as described above. In the latter case, the radical species $\mathrm{A}\cdot^-$ is involved as reductant in the couple $\mathrm{A/A}\cdot^-$, and as oxidant in the couple $\mathrm{A}\cdot^-/\mathrm{A}^{2-}$. If protons are involved in the reaction:

$$26 \qquad \text{oxidant} + n\mathrm{H}^+ + n\mathrm{e}^- \rightarrow \text{reductant}$$

then the reduction potential of the 'half-cell' describing the reaction varies with pH. However, the *standard potential* does *not* vary with pH, since it is defined as the potential referred to the hydrogen standard when each species in the reaction, including H$^+$ if present, is at unit activity. This obviously includes the condition pH = 0 if H$^+$ is a reactant, and leads to considerable confusion. Symbols for standard potentials include $E^{\ominus}$ and E°; the latter is often typeset as E^0 and frequently also expressed as E_0 even though the subscripted symbol does not refer to a standard potential. Obviously, in verbal discussion the opportunities for confusion of E° and E_0 are even greater.

The symbol E_0 is best restricted to denote a *formal* rather than *standard* potential; this distinction should become clear later. Unfortunately, such formal potentials can have rather variable definitions, and care needs to be taken to ascertain just which constants are included in E_0. This point is not always clear even in well-known texts, e.g. Clark's book,[22] and is discussed further below.

4.2. Coupling of Electrons and Protons in the Reaction

Suppose the reductant, formally represented by A^{2-} previously, can be involved in prototropic equilibria, e.g.:

27 $\quad AH_2 \rightleftharpoons AH^- + H^+$

28 $\quad AH^- \rightleftharpoons A^{2-} + H^+$

as can the radical intermediate, $A\cdot^-$ or the oxidant, A:

29 $\quad AH\cdot \rightleftharpoons A\cdot^- + H^+$

30 $\quad AH^+ \rightleftharpoons A + H^+$.

(It is important to recognise that free radicals may have dissociation constants for such equilibria which differ by several orders of magnitude from the corresponding dissociation in the ground state; thus for simple benzoquinones, $pK_{29} \gg pK_{30}$.[3,38]) The two-electron reduction of A to A^{2-} can be represented *either* as *31a*, excluding protons in the equation, *or* as *31b*, which includes protons:

31a $\quad A + 2e^- \rightarrow A^{2-}$

31b $\quad A + 2H^+ + 2e^- \rightarrow AH_2$.

The *standard* potentials, $E^\circ(A/A^{2-})$ and $E^\circ(A, 2H^+/AH_2)$ have quite distinct definitions and values, and when discussing the reduction of A to A^{2-} or its protonated conjugates AH^-, AH_2 we should take care always to qualify E° as shown above with the oxidant/reductant couple in parentheses.

The electrode potential (reduction potential) of a system or couple is the e.m.f. of a cell in which the couple forms the right-hand electrode and the standard hydrogen electrode (s.h.e.) forms the left.[9] If A^{2-} is involved in prototropic equilibria (reactions *27,28*) of any significance over the pH range of practical interest — say 0 to 14 — then the potential of the half-cell in which A is reduced can be assigned the symbol E_h. This is defined in the Nernst relationship:

$$E_h = E^\circ + \frac{RT}{nF}\ln\left\{\frac{\text{(product of activities of oxidant)}}{\text{(product of activities of reductant)}}\right\} \tag{14}$$

where E° is the standard potential of the oxidant/reductant couple *as defined in the half-cell equation*. The relationship can be expressed *either* using the half-cell reaction *31a*:

$$E_h = E^\circ(A/A^{2-}) + \frac{RT}{nF}\ln\frac{(A)}{(A^{2-})} \tag{15}$$

or in terms of the half-cell reaction *31b*, including protons:

$$E_h = E^\circ(A, 2H^+/AH_2) + \frac{RT}{nF}\ln\frac{(A)(H^+)^2}{(AH_2)} \tag{16}$$

whichever is most convenient (see below). (We generally follow the symbols used by Clark,[22] except in the more restrictive use of E_0 as shown below; activities are denoted by parentheses, (A) etc., while concentrations are represented by square brackets, [A] etc.) For simplicity we ignore, for the present, protonation of oxidant (reaction *30*), i.e. $pK_{30} \ll 0$. E_h is *not* a standard potential, but merely the potential of a half-cell in which A is being reduced (in this case by two electrons, ignoring the individual one-electron couples). We *could* use the symbol $E_h(A, 2H^+/AH_2)$ to remind ourselves that the reduction is coupled to protons at some pH values of interest, but the reductant is really a mixture of all three prototropic conjugates.

4.3. General Approach to Describing the pH-Dependence of Reduction Potentials

As noted above, the standard potential $E^\circ(A, 2H^+/AH_2)$ is pH-invariant since the condition $(H^+) = 1$ applies. However, E_h *will* vary with pH since in Eq. (15) the activity of A^{2-} will depend on equilibrium *28* conjugating A^{2-} with H^+. In Eq. (16) not only will (AH_2) be controlled by equilibrium *27*, but (H^+) is also incorporated in the Nernst relationship. The general approach to deriving an expression relating E_h to (H^+) may be summarized: (*i*) Write down the reaction as a reduction of an oxidant to a reductant, reading left to right, in any form in which protons and electrons balance (e.g. reactions *25* or *26*; *31a* or *31b*). (*ii*) Write down the Nernst expression for the reaction as written, with E° clearly defined in parentheses after the symbol (e.g. Eqs. (15) or (16)). (*iii*) Derive expressions for the fraction of total oxidant and/or total reductant which are in the prototropic forms shown in the reaction as written, i.e. in the definition of E°. (*iv*) Substitute these terms in the Nernst expression, and separate out the term for the ratio of total activities (or concentrations, see below) of oxidants and reductants to define a mid-point potential, E_m when this ratio is unity. (*v*) A formal (*not* standard) potential, E_0 can then be defined to separate out the constants and present a relationship between E_m and pH which includes the dissociation constants for the prototropic equilibria involved. The standard potential $E°$ is included in the constant E_0 but the latter may, or may not, approximate to $E°$, as discussed below.

Restricting ourselves for the present to defining E_h for the two-electron reduction of the oxidant A, and ignoring prototropic equilibria such as *30* involving the oxidant, we have already accomplished steps (*i*) and (*ii*) above to arrive at Eqs. (15) and (16). Using Eq. (16), for step (*iii*) we have to derive the proportion of total reductant in the form AH_2. Following Clark,[22] we define the symbol S_r to denote the sum of reductants:

$$S_r = AH_2 + AH^- + A^{2-} \tag{17}$$

and define equilibrium constants for the dissociation of the reductant in decreasing numerical value:

$$K_{r1} = \frac{(AH^-)(H^+)}{(AH_2)} \quad (=K_{27}) \tag{18}$$

$$K_{r2} = \frac{(A^{2-})(H^+)}{(AH^-)} \quad (=K_{28}) \tag{19}$$

We can then express (AH_2) in terms of (S_r), K_{r1} and K_{r2}:

$$(S_r) = (AH_2) + (AH^-) + (A^{2-}) \tag{20}$$

$$(S_r) = (AH_2)\left(1+\frac{K_{r1}}{(H^+)} + \frac{K_{r2}}{(H^+)^2}\right) \tag{21}$$

$$(AH_2) = (S_r)\left(\frac{(H^+)^2}{K_{r1}K_{r2} + K_{r1}(H^+)^2 + (H^+)^2}\right) . \tag{22}$$

To progress to step (*iv*) we define, for consistency, S_o as the sum of the oxidants (only A if we ignore AH^+ formation, reaction *30*). Eq. (16) then becomes:

$$E_h = E°(A,2H^+/AH_2) + \frac{RT}{2F}\ln\frac{(S_0)}{(S_r)} + \frac{RT}{2F}\ln\frac{(K_{r1}K_{r2} + K_{r1}(H^+) + (H^+)^2)(H^+)^2}{(H^+)^2} \tag{23}$$

if we separate out the term with $(S_o)/(S_r)$ since $(S_o) = (A)$. When $(S_o) = (S_r)$, E_h can be described as a 'mid-point' potential with symbol E_m:

$$E_m = E°(A, 2H^+/AH_2) + \frac{RT}{2F}\ln(K_{r1}K_{r2} + K_{r1}(H^+) + (H^+)^2) . \tag{24}$$

Beginning with the alternative 'orienteering reaction' *31a* and its corresponding Nernst relationship Eq. (15), we have to derive an expression for (A^{2-}) analogous to Eq. (22), in a similar fashion:

$$(A^{2-}) = (S_r)\left(\frac{K_{r1}K_{r2}}{K_{r1}K_{r2} + K_{r1}(H^+) + (H^+)^2}\right) . \tag{25}$$

We then obtain the alternative expression for E_m:

$$E_m = E°(A/A^{2-}) + \frac{RT}{2F}\ln\frac{(K_{r1}K_{r2} + K_{r1}(H^+) + (H^+)^2)}{K_{r1}K_{r2}} . \tag{26}$$

Equations (24) and (26) describe the same parameter, E_m, the potential of the half-cell in which A is reduced by 2 electrons when the sum of the activities of the oxidant equals the sum of the activities of the reductant. Equating these expressions, the relationship between the two standard potentials is:

$$E°(A, 2H^+/AH_2) = E°(A/A^{2-}) - \frac{RT}{2F}\ln(K_{r1}K_{r2}) . \tag{27}$$

If potentials are in mV and $T \approx 298$ K:

$$E°(A, 2H^+/AH_2) \approx E°(A/A^{2-}) + 29.6(pK_{r1} + pK_{r2}) . \tag{28}$$

To obtain a more convenient expression for fitting data of E_m vs. pH to the appropriate function, Eq. (26) could be modified by incorporating the pH-independent term, $K_{r1}K_{r2}$ in the denominator, with the standard potential to yield a new constant, E_0:

$$E_0 = E°(A/A^{2-}) - \frac{RT}{2F}\ln(K_{r1}K_{r2}) \tag{29}$$

$$E_m = E_0 + \frac{RT}{2F}\ln(K_{r1}K_{r2} + K_{r1}(H^+) + (H^+)^2) . \tag{30}$$

Clark[22] uses this procedure extensively. However, the definition of E_0 is often not immediately apparent in some more complex situations, and the symbol is very frequently used for a formal potential with a specific definition; this introduces an ambiguity which is discussed below.

4.4. Practical Application to One-Electron Reduction Potentials

Both equilibrium constants and mid-point potentials are usually measurable only in terms of *concentrations* rather than activities, and the expressions for the pH-dependence of E_m for one-electron couples will be derived in terms of these measurable quantities. Consider first the one-electron reduction of A, which can be represented by the two alternative equations:

32a $A + e^- \rightarrow A\cdot^-$

32b $A + H^+ + e^- \rightarrow AH\cdot$.

These are linked by the prototropic equilibrium *29*. The *practical* ionization constant for dissociation of AH· will mix concentrations and activities:

$$K_r' = \frac{[A\cdot^-](\mathrm{H}^+)}{[\mathrm{AH}\cdot]} \quad (=K_{29}') . \tag{31}$$

The use of K' rather than K denotes the use of concentrations for all species except H^+ (activities of H^+ are measured with the glass electrode or calculated using standard buffers). The subscript r with K' is used since A is the oxidant and $AH\cdot/A\cdot^-$ the reductant. Since there is only one ionization of the reductant considered, K_r' rather than K_{r1}' can be used.

The Nernst expression corresponding to the simpler alternative reaction *32a* is:

$$E_h = E°(\mathrm{A/A}\cdot^-) + \frac{RT}{F} \ln \frac{(\mathrm{A})}{(\mathrm{A}\cdot^-)} . \tag{32}$$

When modified to include activity coefficients, f defined by:

$$(\mathrm{A}) = f_\mathrm{A}[\mathrm{A}] \tag{33}$$

etc., this yields:

$$E_h = E°(\mathrm{A/A}\cdot^-) + \frac{RT}{F} \ln \frac{f_\mathrm{A}}{f_{A\cdot^-}} + \frac{RT}{F} \ln \frac{[\mathrm{A}]}{[\mathrm{A}\cdot^-]} . \tag{34}$$

Representing A by S_o and the sum of $A\cdot^-$ and $AH\cdot$ by S_r as before, and following the general approach described above:

$$[\mathrm{A}\cdot^-] = [S_r]\left(\frac{K_r'}{K_r' + (\mathrm{H}^+)}\right) \tag{35}$$

$$E_h = E°(\mathrm{A/A}\cdot^-) + \frac{RT}{F} \ln \frac{f_\mathrm{A}}{f_{\mathrm{A}\cdot^-}} + \frac{RT}{F} \ln \frac{[S_o]}{[S_r]} + \frac{RT}{F} \ln \left(\frac{K_r' + (\mathrm{H}^+)}{K_r'}\right). \tag{36}$$

If a *formal potential*, E_0 is now defined as the midpoint potential when the ratio of the total concentrations of oxidized and reduced species is unity, and H^+ is at unit activity (pH = 0), then from Eq. (36):

$$E_0 = E°(\mathrm{A/A}\cdot^-) + \frac{RT}{F} \ln \frac{f_\mathrm{A}}{f_{\mathrm{A}\cdot^-}} + \frac{RT}{F} \ln \left(\frac{K_r' + 1}{K_r'}\right). \tag{37}$$

$$E_m = E_0 + \frac{RT}{F} \ln \left(\frac{K_r' + (\mathrm{H}^+)}{K_r' + 1}\right). \tag{38}$$

For many species of interest, such as semiquinones, $K_r' \ll 1$ so that:

$$E_0 \approx E°(\mathrm{A/A}\cdot^-) + \frac{RT}{F} \ln \frac{f_\mathrm{A}}{f_{\mathrm{A}\cdot^-}} - \frac{RT}{\mathrm{F}} \ln K_r' \tag{39}$$

$$E_m \approx E_0 + \frac{RT}{F} \ln (K_r' + (\mathrm{H}^+)) . \tag{40}$$

The latter two equations also result if E_0 has no specific definition but merely represents taking out the pH-independent terms in the expressions for E_h or E_m. The values of E_0 calculated from Eq. (39) rather than Eq. (37) may differ by negligibly small amounts, e.g. by 0.3 mV if $pK_r' > 2$; however, it is recommended that E_0 is defined clearly as the formal potential described above even though it introduces extra terms such as $(K_r' + 1)$ in the equations. We can then use consistently subscripts with E_m to denote pH and by definition, $E_{m0} = E_0$.

Equation (38) may also be derived starting from the alternative Nernst relationship corresponding to reaction *32b*:

$$E_h = E°(\mathrm{A, H^+/AH\cdot}) + \frac{RT}{F} \ln \frac{(\mathrm{A})(\mathrm{H}^+)}{(\mathrm{AH}\cdot)} . \tag{41}$$

An expression is derived for [AH·] in terms of $[S_r]$, etc., except that E_0 in Eq. (38) now becomes (using the defined formal potential as before):

$$E_0 = E°(\mathrm{A, H^+/AH\cdot}) + \frac{RT}{F} \ln \frac{f_\mathrm{A}}{F_{\mathrm{AH}\cdot}} + \frac{RT}{F} \ln (K_r' + 1). \tag{42}$$

At constant ionic strength, Eqs. (37) and (42) equate, so that

$$E°(\mathrm{A/A}\cdot^-) = E°(\mathrm{A,H^+/AH\cdot}) + \frac{RT}{F} \ln \frac{f_\mathrm{A}}{f_{\mathrm{AH}\cdot}} \frac{RT}{F} \ln k_r' . \tag{43}$$

Since:

$$K_r' = K_r \frac{f_{\mathrm{A}\cdot^-}}{f_{\mathrm{AH}\cdot}} \tag{44}$$

$$E°(\mathrm{A/A}\cdot^-) - E°(\mathrm{A, H^+/AII\cdot}) + \frac{RT}{F} \ln K_r . \tag{45}$$

This relationship may be re-arranged in the same form as Eq. (28):

$$E°(\mathrm{A, H^+/AH\cdot}) \approx E°(\mathrm{A/A}\cdot^-) + 59.2\ pK_r . \tag{46}$$

Obviously, Eq. (45) may also be derived more directly in the same way as was Eq. (27), using activities rather than concentrations, or by simply considering the free-energy changes in the reactions concerned.

Note that E_0 as defined by Eq. (42) does not equate to $E°(\mathrm{A,H^+/AH\cdot})$, but if $K_r' \ll 1$ it *approximates* to it at low ionic strength. These formal potentials may be defined to include not only activity coefficients, but also e.g. complexation with counter-ions in the supporting electrolyte. Thus for the Fe(III)/Fe(II) couple, E_0 is dependent upon the nature of the acid as well as ionic strength. An extension of this approach is to define the formal potential to have some other 'standard' condition (really, non-standard!). For example, in biochemical systems (H^+) may be redefined with pH = 7 as the 'standard' state; a symbol such as E_0' may then be used.

Regardless of the definition of E_0, at any two pH values, i and j, Eq. (38) yields:

$$E_{mi} = E_{mj} + \frac{RT}{F} \ln \left(\frac{K_r' + 10^{-i}}{K_r' + 10^{-j}} \right). \qquad (47)$$

For the radical/reductant one-electron couple, the half-cell may be written in several forms:

33a $A\cdot^- + e^- \rightarrow A^{2-}$

33b $A\cdot^- + H^+ + e^- \rightarrow AH^-$

33c $A\cdot^- + 2H^+ + e^- \rightarrow AH_2$

33d $AH\cdot + H^+ + e^- \rightarrow AH_2.$

The Nernst expression for reaction *33a* is:

$$E_h = E^\circ(A\cdot^-/A^{2-}) + \frac{RT}{F} \ln \frac{(A\cdot^-)}{(A^{2-})}. \qquad (48)$$

The radical species $AH\cdot/A\cdot^-$ is now the oxidant, rather than the reductant as in the example immediately preceding. Thus we denote:

$$K_o' = \frac{[A\cdot^-](H^+)}{[AH\cdot]} \quad (= K_{29}') \qquad (49)$$

(cf. (Eq. 31)), and

$$[A\cdot^-] = [S_o] \left(\frac{K_o'}{K_o' + (H^+)} \right) \qquad (50)$$

(cf. (Eq. 35)). The reductant concentration, $[A^{2-}]$ is defined by Eq. (22) except that concentrations replace activities and practical ionization constants K_{r1}', K_{r2}' are used. We then obtain:

$$E_0 = E^\circ(A\cdot^-/A^{2-}) + \frac{RT}{F} \ln \frac{f_{A\cdot^-}}{f_{A^{2-}}} + \frac{RT}{F} \ln \left(\frac{K_o'}{K_o' + 1} \right) + \frac{RT}{F} \ln \left(\frac{K_{r1}'K_{r2}' + K_{r1}'(H^+) + (H^+)^2}{K_{r1}'K_{r2}'} \right). \qquad (51)$$

If the formal potential, E_0 is defined strictly as before, with unit ratio of total concentrations of oxidant to reductant, and $(H^+) = 1$, then:

$$E_0 = E^\circ(A\cdot^-/A^{2-}) + \frac{RT}{F} \ln \frac{f_{A\cdot^-}}{f_{A^{2-}}} + \frac{RT}{F} \ln \left(\frac{K_o'}{K_o' + 1} \right) + \frac{RT}{F} \ln \left(\frac{K_{r1}'K_{r2}' + K_{r1}' + 1}{K_{r1}'K_{r2}'} \right). \qquad (52)$$

$$E_m = E_0 + \frac{RT}{F} \ln \left(\frac{K_{r1}'K_{r2}' + K_{r1}'(H^+) + (H^+)^2}{K_o' + (H^+)} \right) + \frac{RT}{F} \ln \left(\frac{K_o' + 1}{K_{r1}'K_{r2}' + K_{r1}' + 1} \right). \qquad (53)$$

The last term in Eq. (53) will be negligible if K_o', K_{r1}', $K_{r2}' \ll 1$. Indeed, as noted above, it would be omitted if E_0 was simply defined by combining the pH-independent terms in Eq. (51).

Corresponding pairs of expressions for E_0 and E_m are derived setting out from the alternative orienteering reactions *33b-d*. The standard potentials are related by:

$$E^\circ(A\cdot^-/A^{2-}) = E^\circ(A\cdot^-, H^+/AH^-) + \frac{RT}{F} \ln K_{r2} \qquad (54a)$$

$$= E^\circ(A\cdot^-, 2H^+/AH_2) + \frac{RT}{F} \ln K_{r1}K_{r2} \qquad (54b)$$

$$= E^\circ(AH\cdot, H^+/AH_2) + \frac{RT}{F} \ln \frac{K_{r1}K_{r2}}{K_o}. \qquad (54c)$$

These relationships, and also Eqs. (27) and (45) can be most simply obtained by writing down the appropriate equations and summing the free energy changes involved.

Again, for any two pH values, i and j, Eq. (51) or Eq. (53) yields:

$$E_{mi} = E_{mj} + \frac{RT}{F} \ln \left(\frac{K_{r1}'K_{r2}' + K_{r1}'(10^{-i}) + 10^{-2i}}{K_{r1}'K_{r2}' + K_{r1}'(10^{-j}) + 10^{-2j}} \right) + \frac{RT}{F} \ln \left(\frac{K_o' + 10^{-j}}{K_o' + 10^{-i}} \right). \qquad (55)$$

We neglected earlier the possibility of protonation of the oxidant, A as in equilibrium *30*. Returning to the one-electron reduction of A, to incorporate this equilibrium we define:

$$K_o' = \frac{[A](H^+)}{[AH^+]} \quad (= K_{30}'). \qquad (56)$$

Following the usual approach we obtain, for example:

$$E_i = E_j + \frac{RT}{F} \ln \left(\frac{K'_r + 10^{-i}}{K'_r + 10^{-j}} \right) \left(\frac{K'_o + 10^{-j}}{K'_o + 10^{-i}} \right). \qquad (57)$$

This describes the variation with pH of the mid-point potential of the oxidant/radical one-electron couple, in place of Eq. (47).

4.5. Examples of the pH-Dependence of One-Electron Reduction Potentials and Suggestions for Symbols

The quinone/semiquinone and semiquinone/hydroquinone one-electron couples are illustrated in Figs. 1 and 2 respectively. The mid-point potentials, E_m are plotted *vs.* pH for 1,4-benzoquinone. (The numerical values used are those calculated in Sec. 5.5, below). The pH range 0-14 is separated into regions with pK values defining the 'break points'. In each region, the prototropic forms of the species *predominating* are shown in a box: oxidant, upper species; reductant, lower. The positions of the various standard potentials, E° are also given. It should be stressed that the apparent coincidence of some standard potentials with intercepts (pH 0) or asymptotes (pH $\approx$ 14) in the curves of E_m *vs*. pH arises because of the identity: $0 \leqslant (\mathrm{p}K_s, \mathrm{p}K_{r1}, \mathrm{p}K_{r2}) \leqslant 14$ *in this example*, and not by definition ($\mathrm{p}K_s = \mathrm{p}K_a$ for dissociation of the semiquinone species, QH·).

It has been stressed already that E° should always be qualified with the half-cell reaction in parenthesis, as shown in Figs. 1 and 2, and that E_0 is to be preferred as a defined, formal potential rather than a collection of constants. However, convenient abbreviations to qualify E_m are not so simply defined; perhaps it is reasonable to use the prototropic forms predominating over the pH range of most interest. Thus the abscissae in Figs. 1 and 2 might be labeled: $E_m(\mathrm{A/A\cdot^-})$ and $E_m(\mathrm{Q\cdot^-, 2H^+/QH_2})$ respectively. We stress again that E° does *not* vary with pH.

It has been common practice to use superscripts to qualify symbols for first and second one-electron reduction potentials, with subscripts for pH, e.g. $E^1_7(\mathrm{A/A\cdot^-})$ or $E^2_{13.5}(\mathrm{A\cdot^-/A^{2-}})$. This now seems superfluous and possibly confusing. On the other hand, if results are described as mid-point potentials throughout (except where standard potentials are clearly denoted), it seems reasonable to use E_i for simplicity rather than E_{mi}, where the subscript i is the pH.

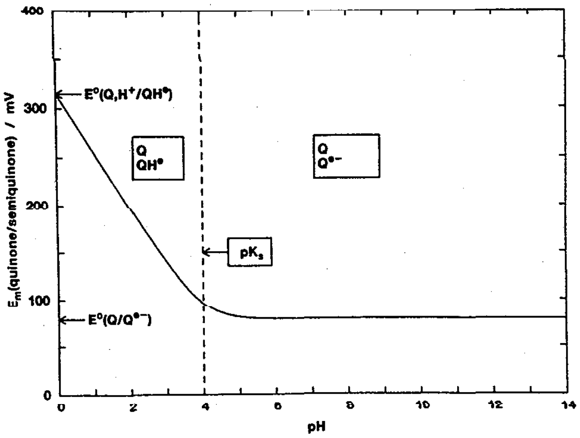

FIG. 1. Variation of the mid-point potential, E_m with pH of the one-electron couple: quinone/semiquinone for 1,4-benzoquinone.

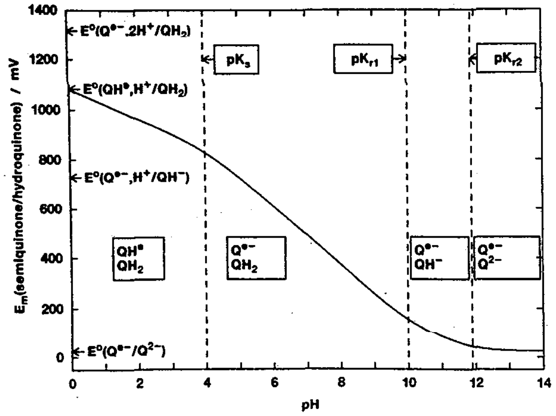

FIG. 2. Variation of the mid-point potential, E_m with pH of the one-electron couple: semiquinone/hydroquinone for 1,4-benzoquinone

The variation of E_m with pH may be influenced by prototropic functions not closely associated with the redox center, if the pK_a of the function differs in oxidant and reductant. Figure 3 shows an example of the effect of a basic function in the substituent in a nitroaryl compound. The unsubstituted imidazolyl nitrogen has $pK_a \leqslant 0$ in the ground state and may be ignored. However, this site is protonated in the electron adduct (radical), with $pK'_{r1} \approx 5.0$. The piperidino nitrogen in the substituent protonates with $pK'_0 \approx 7.6$ in the ground state, but the inductive effect of the nitroaryl group is reduced in the electron-adduct: $pK'_{r2} \approx 8.5$ fits the experimental data. This shift in pK_a of ~ 0.9 is observed in spite of an 'insulating' saturated carbon chain separating the basic site and the redox center. (In this example, the nitro group will be protonated in the radical, but this occurs at pH values lower than those shown.)

Similarly, other unpublished work by the author indicates the carboxylate function in 4-nitrobenzoic acid dissociates with a pK_a about 0.9 higher in the radical-ion than the ground state. Such effects, if ignored, result in significant errors in extrapolating to lower pH values. They may be present to some extent, although as yet undetected, in biologically-important redox couples involving tryptophan and tyrosine, for example.

4.6. The Use of Mid-Point Potentials in Calculating Equilibrium Constants

The Introduction (Sec. 1) showed how reduction potentials were related to electron-transfer equilibria such as *1*:

1 $$A\cdot^- + B \rightleftharpoons A + B\cdot^- .$$

If A, B and/or the radicals, $A\cdot^-$, $B\cdot^-$ are involved in prototropic equilibria, then the measured mid-point potentials E_{mi} will yield, *via* Eq. (5), an apparent or *effective* equilibrium constant, K_i where:

$$K_i \approx \left(\frac{[S_A][S_{B\cdot^-}]}{[S_B][S_{A\cdot^-}]}\right). \qquad (4')$$

This is a modification of Eq. (4) where, following previous use, we replace [A], $[A\cdot^-]$, etc. by the sums of the concentrations of related prototropic conjugates: $[S_{A\cdot^-}] = ([A\cdot^-] + [AH\cdot])$, etc. Such an effective equilibrium constant is most useful in predicting the overall equilibrium, or direction of electron flow, as illustrated in Fig. 4.

This figure represents an equilibrium *1* in which, like semiquinones for example, the reductant species $A\cdot^-$, $B\cdot^-$ participate in prototropic equilibria, with $E°(A/A\cdot^-)$ and $E°(B/B\cdot^-) = -400$ and -300 mV respectively but with pK_a for the dissociation of the protonated conjugates, $AH\cdot$ and $BH\cdot = 8$ and 5 respectively. At pH $\geqslant 9$, K_i can be calculated from Eqs. (1) and (5) to be ≈ 49. However, because E_{mi} increases more rapidly with decreasing pH for the oxidant A compared to B, the *effective* position of the equilibrium reverses at pH $\leqslant 6$. At pH $\leqslant 4$, K_i is approximately constant at ≈ 0.05.

It is preferable to treat such pH-dependent equilibria in this way rather than add protons to equilibrium *1* and work with complex equilibrium expressions. There is, however, an important *kinetic* consequence of these prototropic equilibria in many instances. It is commonly observed that protonation (or absence of ionization) of

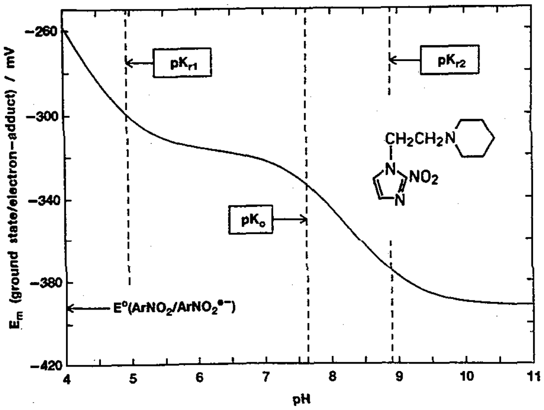

FIG. 3. Variation of the mid-point potential, E_m with pH of the one-electron reduction potential of 1-(2-piperidinylethyl)-2-nitroimidazole ($ArNO_2$)

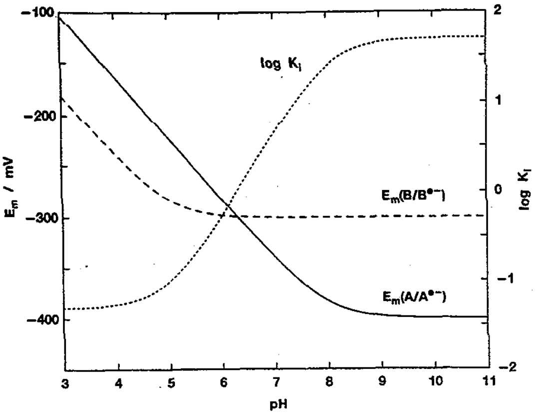

FIG. 4. Variation of the mid-point potentials, E_m with pH of the one-electron couples of two hypothetical oxidants A and B (see text) and the logarithm of the effective equilibrium constant K_i for the one-electron transfer equilibrium between these oxidants and their electron-adducts

basic (or acidic) functions slows down the rates of electron transfer reactions, often dramatically, as noted in Sec. 3.5. The *rate* of approach to equilibrium *1* may depend, for example, on the fraction of radicals from A present in the form $A\cdot^-$ rather than the much less reactive $AH\cdot$. Thus the electron-transfer equilibrium *1* may not be kinetically achievable under practicable conditions even though calculation readily establishes the thermodynamic feasibility. In general, prototropic equilibria are established so rapidly that the kinetics of proton transfer are seldom rate-determining.

Other, some more complex, illustrations of the effects of prototropic equilibria on reduction potentials have been discussed, e.g. for quinones,[6,39-42] nitroaromatic compounds,[7] flavins,[43] phenoxyl radicals,[8] etc. The principles of the calculations are simply as outlined above in Sec. 4.3. In some instances, however, the formulae given represent approximations to those derived herein. In almost every case the practical implications of such differences are negligible.

5. Calculation of One-Electron Reduction Potentials Using Radical Formation Constants

5.1. Introduction

Radicals, e.g. $A\cdot^-$ may be present in equilibrium with oxidant, A and reductant, A^{2-} or their protonated conjugates:

34 $\qquad A + A^{2-} \rightleftharpoons 2\,A\cdot^-$

and a radical formation constant can be defined:

$$K_f = \frac{(A\cdot^-)^2}{(A)(A^{2-})}\,. \tag{58}$$

The value of K_f is obviously a measure of the steady-state concentrations of radicals, $A\cdot^-$ obtained on mixing oxidant A with reductant, A^{2-}. When experimental conditions result in sufficiently high concentrations of radicals to be measured, estimates of K_f can be used in conjuction with the two-electron potentials, $E^\circ(A/A^{2-})$ or $E^\circ(A, 2H^+/AH_2)$ to obtain estimates of the one-electron couples, $E^\circ(A/A\cdot^-)$, etc.

5.2. Derivation of Expressions

Reaction *34* (above) can be obtained by subtracting *33a* from *32a*:

32a $\qquad A + e^- \rightarrow A\cdot^-$

33a $\qquad A\cdot^- + e^- \rightarrow A^{2-}\,.$

Eq. (59) is obtained by subtracting the corresponding free-energy changes:

$$E^\circ(A/A\cdot^-) - E^\circ(A\cdot^-/A^{2-}) = \frac{RT}{F}\ln K_f. \tag{59}$$

If we add reaction *32a* to reaction *33a* we obtain reaction *31a*. Noting that $n = 2$ in the conversion of free energy to potential, Eq. (2), in the latter reaction:

$$E^\circ(A/A\cdot^-) + E^\circ(A\cdot^-/A^{2-}) = 2\,E^\circ(A/A^{2-}) \tag{60}$$

(cf. Eq. (6)). Adding Eqs. (59) and (60) yields:

$$E^\circ(A/A\cdot^-) = E^\circ(A/A^{2-}) + \frac{RT}{2F}\ln K_f \tag{61}$$

while subtraction gives:

$$E^\circ(A\cdot^-/A^{2-}) = E^\circ(A/A^{2-}) - \frac{RT}{2F}\ln K_f. \tag{62}$$

Using Eq. (28) with potentials in mV and $T \simeq 298$ K:

$$E^\circ(A/A\cdot^-) \approx E^\circ(A, 2H^+/AH_2) - 29.6(pK_{r1} + pK_{r2} + pK_f) \tag{63}$$

$$E^\circ(A\cdot^-/A^{2-}) \approx E^\circ(A, 2H^+/AH_2) - 29.6(pK_{r1} + pK_{r2} - pK_f) \tag{64}$$

where K_{r1}, K_{r2} are the dissociation constants for AH_2 and AH^- respectively as defined in Eqs. (18) and (19).

It may be difficult to measure K_f directly, e.g. because very high pH values may be required to ionize completely the reductant to A^{2-}. It is much more convenient to define an apparent formation constant, $K_{f\,i}$ at an experimentally accessible pH, i:

$$K_{f\,i} = \frac{(S_s)^2}{(S_o)(S_r)}\,. \tag{65}$$

We follow previous symbolism and define S_o and S_r as the sums of the oxidant (only A) and reductant ($AH_2 + AH^- + A^{2-}$) respectively, as before, and use S_s to represent the sum of the radical intermediate species. The subscript s is convenient because the radical will be a semiquinone in many examples. It is easily shown, using the approach already used in Sec. 4.3, that:

$$K_f = K_{f\,i}\left(\frac{K_S}{K_S + (H^+)}\right)\left(\frac{K_{r1}K_{r2} + K_{r1}(H^+) + (H^+)^2}{K_{r1}K_{r2}}\right) \tag{66}$$

where K_{r1}, K_{r2} are defined in Eqs. (18) and (19) as before and $K_s = K_{29}$.

As noted earlier, in practice, concentrations rather *than* activities are generally measured. We will usually obtain an estimate of K_f or $K_{f\,i}$ at some ionic strength, I. Using K_f', $K_{f\,i}'$ as before to denote the apparent formation constants thus defined in *concentration* terms except for (H^+), together with the mid-point potentials E_{mi} measured at the same ionic strength, it can be shown that:

$$E_{\mathrm{m}i}(\mathrm{A}/\mathrm{A}\cdot^{-}) = E_{\mathrm{m}i}(\mathrm{A}/\mathrm{A}^{2-}) + \frac{RT}{2F}\ln K'_{\mathrm{f}\,i} \qquad (67)$$

$$E_{\mathrm{m}i}(\mathrm{A}\cdot^{-}/\mathrm{A}^{2-}) = E_{\mathrm{m}i}(\mathrm{A}/\mathrm{A}^{2-}) - \frac{RT}{2F}\ln K'_{\mathrm{f}\,i}\,. \qquad (68)$$

The mid-point condition now refers to the sum of the *concentrations* of oxidant being equal to the sum of the concentrations of reductant. (The activity coefficient terms in Eqs. (36) and (51) cancel out the terms in Eq. (69)).

$$K'_{\mathrm{f}} = K_{\mathrm{f}}\frac{f^2_{\mathrm{A}\cdot^{-}}}{f_{\mathrm{A}}f_{\mathrm{A}^{2-}}}\,. \qquad (69)$$

5.3. Examples of Calculations

The one-electron reduction potential of the oxidant, duroquinone (DQ) can be *estimated* using electrochemical data for the reduction potential of the two-electron couple: duroquinone/durohydroquinone, and spectrophotometric measurement of the semiquinone concentration present in mixtures of the quinone and hydroquinone at high pH. Interpolating Baxendale and Hardy's data[44,45] to yield values at 298 K give: $\mathrm{p}K'_{\mathrm{r1}} = 11.24$, $\mathrm{p}K'_{\mathrm{r2}} = 12.83$ and $\mathrm{p}K'_{\mathrm{f}} = 0.11$ at $I = 0.65$. Conant and Fieser[47] indicate $E^\circ(\mathrm{DQ,2H^+/DQH_2}) = 480$ mV (but used 50% ethanol). Equation (63) then yields an *estimate* of $E^\circ(\mathrm{DQ/DQ}\cdot^{-}) = -236$ mV, ignoring the use of practical rather then thermodynamic equilibrium constants. Alternatively, Michaelis et al.[48] estimated $E_{\mathrm{m}i}$(duroquinone/durohydroquinone) using 20% pyridine in water at 303 K, for pH (i) = 7.4 to 13.5; a value of $E_{\mathrm{m}7} = 41$ mV is interpolated. Baxendale and Hardy's data,[44,45] and $\mathrm{p}K'_{\mathrm{s}} = 5.1$ from pulse radiolysis,[3] yields $K'_{\mathrm{f}7} = 1.1 \times 10^{-10}$. Using Eq. (67), $E_7(\mathrm{DQ/DQ}\cdot^{-}) = -254$ mV is *estimated*. These values are similar to those obtained quite independently by Wardman and Clarke[32] using pulse radiolysis.

(A number of authors have used $\mathrm{p}K'_{\mathrm{r2}} = 13.2$ for duroquinone, as tabulated from Bishop and Tong[46] from Baxendale and Hardy's measurements. The original data[44] clearly show $\mathrm{p}K'_{\mathrm{r2}}$ varying between 13.17 at 14.9 °C to 12.70 at 29.8 °C, from which the present author interpolates a value of 12.83 at 298 K).

Electron spin resonance measurements[49] of the steady-state concentrations of ascorbyl radicals produced on mixing the reductant, ascorbic acid with the corresponding oxidant, dehydroascorbic acid gave estimates of $K_{\mathrm{f}i}$ between pH 4.0 and 6.4. An *estimate* of $K_{\mathrm{f}} = 1.2 \times 10^{-3}$ is obtained using Eq. (66) and $\mathrm{p}K'_{\mathrm{r1}} = 4.21$, $\mathrm{p}K'_{\mathrm{r2}} = 11.52$ (representative literature values) and $\mathrm{p}K_{\mathrm{s}} = -0.45$.[50] A value of $E_{\mathrm{m}0} = 400$ mV for the two-electron reduction (see Clark,[22] p.470), will be close to $E^\circ(\mathrm{A,\ 2H^+/AH_2})$, from Eq. (24). Eq. (64) yields $E^\circ(\mathrm{A}\cdot^{-}/\mathrm{A}^{2-}) \approx 19$ mV for A^{2-} = ascorbic acid. Steenken and Neta,[8] using the pulse radiolysis redox equilibrium method, estimated $E_{13.5}(\mathrm{A}\cdot^{-}/\mathrm{A}^{2-}) = 15$ mV. This is well within the uncertainty of the independent calculation. (Because $\mathrm{p}K'_{\mathrm{r2}} \approx 11.5$, $E_{13.5}(\mathrm{A}\cdot^{-}/\mathrm{A}^{2-}) \approx E^\circ(\mathrm{A}\cdot^{-}/\mathrm{A}^{2-})$).

5.4. Uncertainties In the Calculations

As an example, consider the calculation for $E^\circ(\mathrm{A/A}\cdot^{-})$ for A = simple quinones. Clark's tables[22] of values of E_0 for the two-electron reduction of many quinones indicate random uncertainties of 5-15 mV, the higher values including measurements in partly non-aqueous solvents. In these cases E_0 *approximates* to $E^\circ(\mathrm{A,\ 2H^+/AH_2})$. To calculate the uncertainty in the estimate of $E^\circ(\mathrm{A/A}\cdot^{-})$, for example, we also need to consider the uncertainty in the sum: $\mathrm{p}K_{\mathrm{r1}} + \mathrm{p}K_{\mathrm{r2}} + \mathrm{p}K_{\mathrm{f}}$, as indicated in Eq. (63). Estimates[44-46] of $\mathrm{p}K'_{\mathrm{r1}}$, $\mathrm{p}K'_{\mathrm{r2}}$ and $\mathrm{p}K'_{\mathrm{f}}$ refer to ionic strengths of 0.65 or 0.375, and the substitution of these practical constants for the thermodynamic constants required in Eq. (63) introduces *systematic* errors.

Perrin *et al.*[51] derived a formula to correct practical ionization constants. For dissociation of the weak acid $\mathrm{HA}^{(n-1)-}$:

35 $$\mathrm{HA}^{(n-1)-} \rightleftharpoons \mathrm{A}^{n-} + \mathrm{H}^{+}$$

$$\mathrm{p}K \approx \mathrm{p}K' + [(2n-1)/2]f(I). \qquad (70)$$

We have adapted his formula to use the ionic strength function, $f(I)$ previously defined:

$$f(I) \approx 1.02(I^{\frac{1}{2}}(1 + I^{\frac{1}{2}})^{-1} - 0.2I). \qquad (13)$$

At high ionic strengths, $I \approx 0.4\text{-}0.6$, reliable use of Eq. (70) is doubtful. However, we see that for uncharged quinones (e.g. duroquinone), $\mathrm{p}K'_{\mathrm{r1}}$ and $\mathrm{p}K'_{\mathrm{r2}}$ may *under*estimate the thermodynamic values by *ca.* 0.1-0.2 and 0.5 respectively. It can be shown that

$$\mathrm{p}K_{\mathrm{f}} \approx \mathrm{p}K'_{\mathrm{f}} - f(I) \qquad (71)$$

for uncharged oxidants A, i.e. for uncharged quinones. The semiquinone formation constant decreases with increasing I so that $\mathrm{p}K'_{\mathrm{f}}$ *over*estimates $\mathrm{p}K_{\mathrm{f}}$ by *ca.* 0.3 at $I \approx 0.4\text{-}0.6$. There is thus partial canceling-out of these systematic errors in the application of Eq. (63). The systematic error introduced into the calculation of $E^\circ(\mathrm{A/A}\cdot^{-})$ will still amount to the estimate being *ca.* 10 mV more positive than the true value.

Even for these simple quinones, generally only one estimate[44-46] of the ionization and formation constants required is available. *Even discounting random errors* in their determination, the calculations of one-electron reduction potential as described in this section must involve uncertainties of *at least* 10-20 mV is general. Similar consideration may be given to other applications of the formulae derived.

These illustrations may be used, in turn, to refine calculations of standard potentials using experimental measurements of ionization and formation constants. Thus the literature data [illegible] for 1,4-benzoquinone may be corrected to yield estimates of the thermodynamic constants pK_{a1}, pK_{a2}, pK_{r1} and pK_{r2} of 10.0, 11.9, 4.0 and -0.92 respectively. Using the well-established[22] $E°(Q,2H^+/QH_2) = 699$ mV yields estimates of $E°(Q,Q\cdot^-) = 78$ mV and $E°(Q\cdot^-, Q^{2-}) = 24$ mV, the former some 20 mV lower than previous estimates.[42] In fact, such corrections are not so straight-forward, since Baxendale and Hardy[44] included some activity coefficients (of the buffers used) in defining K'_{r1}, K'_{r2}. The simple application of Eqs. (70) or (71) may be inappropriate in some instances.

6. Recommended Redox Indicators and Their Potentials

The choice of redox indicators B with which to establish and measure the position of the desired equilibrium *1* with the unknown A is influenced by several factors. Ideally, determinations of K_1 with two indicators — one higher than the unknown by (say) 50-100 mV, one lower — will lead to the most reliable value. In practice, the choice depends on solubilities, absorption spectra of reactants and products, pK_a's, kinetic constraints, (especially the need for fast electron transfer, see above, Sec. 3.5) and ready availability with adequate purity.

6.1. Oxygen

Oxygen is an important reactant with many radicals, although electron-transfer rather than radical-addition is a pre-requisite and it is somewhat inconvenient to vary the concentration of oxygen over a wide range. It is useful to draw attention again to the standard definition: $E°(O_2(1\ \text{atm.})/O_2\cdot^-) = -325$ mV whereas $E(O_2(1\ \text{mol dm}^{-3})/O_2\cdot^-) = -155$ mV.

6.2. Quinones

Reduction potentials for the couples $A/A\cdot^-$ and $A\cdot^-/A^{2-}$ for A = quinones may be calculated[4,5,6,42] from the ionization constants of AH_2 and the semiquinone formation constants, as described above (Sec. 5). Completely independent estimates of $E°(A/A\cdot^-)$ for A = *duroquinone* are provided by the measurements of ΔE_1 corrected to $I = 0$ for A = duroquinone and B = 1,1'-dibenzyl-4,4'-bipyridinium dication.[32] Values of ΔE_1 of 110 ± 4[32], 113 ± 4[52], and 107 ± 3[53] mV together with $E°(B/B\cdot^-) = -354$ mV (but see below, Sec. 6.3) yield $E°(A/A\cdot^-) = -244$ mV for duroquinone, in good agreement with the values calculated[4,5,6,42] from dissociation constants (see also Sec. 5.3). A value of $E°(A/A\cdot^-) = -375$ mV for *9,10-anthraquinone-2-sulfonate* is a reasonable mean of estimates based on equilibria involving duroquinone[7,32,52], and two bipyridinium indicators [32,52,53] and is quite close to the value -360 mV obtained polarographically at high pH.[24] The more negative potential now recommended for benzyl viologen (see below) will result in corresponding alterations to the values for the quinone couples, e.g. to -260 mV for duroquinone and -390 mV for 9,10-anthraquinone-2-sulfonate.

Reduction potentials for other quinone couples have been calculated[4,5,6,42] from literature data and experimentally derived[43] from equilibrium measurements. They can be relied upon when confirmed by independent routes, e.g. when the values are consistent with measurements of the $A\cdot^-/O_2$ equilibrium.[5,6,43] 1,4-Benzoquinone (Q) is a recommended standard, with $E°(Q/Q\cdot^-) = 78$ mV and $E°(Q\cdot^-/Q^{2-}) = 24$ mV, as calculated in Sec. 5.4.

6.3. Bipyridinium Compounds (Viologens)

While these viologens are, in principle, excellent redox indicators because the radicals $A\cdot^-$ are essentially stable in aqueous solution and have a high extinction coefficient at wavelengths where interfering absorptions are seldom a problem, a note of caution is appropriate. Not only is variable water of hydration a problem (relatively minor in this context) with the dimethyl derivative (paraquat), but variable purity of commercial samples of both viologens has been noted. Note, however, that the spectra of the viologen radical cations are concentration-, temperature- and time-dependent[32,54-59] and that electrochemical measurements may involve higher concentrations of these cations than are utilized in pulse radiolysis measurements. The spectral changes arise because the radical cations $V\cdot^+$ obtained on one-electron reduction of viologens, V^{2+} dimerize:

36 $$(V\cdot^+)_2 \rightleftharpoons V\cdot^+ + V\cdot^+.$$

Estimates of the apparent dimer dissociation constant, K'_D have been made. These vary from $\sim 1.5 \times 10^{-3}$ mol dm^{-3} for methyl viologen[55-57] to $\sim 2.7 \times 10^{-3}$ (ethyl viologen)[58] and 2×10^{-5} mol dm^{-3} (benzyl viologen),[59] *under the experimental conditions used* (K'_D is ionic strength dependent). If x is the fraction of radicals in the monomeric form and S_r is the total concentration of reductant ($[V\cdot^+] + 2[(V\cdot^+)_2]$), then:

$$K'_D = \frac{2S_r x^2}{(1-x)}. \tag{72}$$

The $\sim$100-fold lower value of K_D for benzyl viologen compared to its methyl analogue has serious implications in using the former as a redox indicator, since it is seen that if e.g. $S_r = 10^{-5}$ mol dm^{-3}, $x \approx 0.6$ with benzyl viologen. By application of the Nernst relationship in a similar manner to that used in Sec. 4, it can be shown that:

$$E_m = E°(V^{2+}/V\cdot^+) - \frac{RT}{F}\ln\left\{\frac{K_D}{4S_r}([1 + (8S_r/K_D)]^{\frac{1}{2}} - 1)\right\}. \tag{73}$$

If, e.g. $K_D = 5 \times 10^{-5}$ mol dm^{-3} and $S_r = 2.5 \times 10^{-4}$ mol dm^{-3}, E_m is *ca.* 30 mV more positive than $E°(V^{2+}/V\cdot^+)$.

Concentration-dependent mid-point potentials for benzyl viologen (BV^{2+}) have been reported[60-61] and it seems likely that the value of this reference potential is more negative than the electrochemical data suggest.[61] A provisional value of −370 mV would be reasonable, pending further investigation; such a value is also consistent with unpublished work by the author with Mr. E.D. Clarke. Experiments determining ΔE for nitroaryl compounds vs. both benzyl and methyl viologen indicated *either* $E°(V^{2+}/V\cdot^+)$ for the benzyl analogue was lower than −354 mV (previously assumed) *or* the value for methyl viologen was higher than the well-established value of −448 mV. The apparent correction necessary was usually ~16 mV, in agreement with the new recommendation for $E°(BV^{2+}/BV\cdot^+) = -370$ mV.

This problem of dimerization of viologen radical-cations has serious implications in estimating the value of $E°(BV^{2+}/BV\cdot^+)$ from electrochemical measurements. It is much less of a problem when electron-transfer equilibria with $BV\cdot^+$ as reactant are studied by pulse radiolysis, since $[BV\cdot^+]$ is typically $\leqslant 1$ μmol dm^{-3} at equilibrium, and the equilibrium point may well be established before significant dimerization (reverse of reaction *36*) can occur. Dimerization is also much less of a problem with methyl viologen (MV^{2+}), and there are so many values published (see Table 3, compound 3.8.2) that outliers can be clearly identified. A value of $E°(MV^{2+}/MV\cdot^+) = -448$ mV is recommended. The usefulness of low potential viologens in particular, outweigh these uncertainties. The reported[62] protonation of the methyl viologen radical cation with $pK_a = 1$ seems more likely ascribable to other reactions[63], and the pH-independence of these couples is a further advantage.

6.4. Hydroquinones and Phenols

The studies of Steenken and Neta[8,64] of equilibria of the form:

$$A\cdot^- + B^{2-} \rightleftharpoons A^{2-} + B\cdot^- \qquad (37)$$

with A^{2-}, B^{2-} = hydroxy- and amino-phenols, phenylenediamines, etc. have provided values of $E_{13.5}(A\cdot^-/A^{2-}) = 23$, 43 and 174 mV for A^{2-} = hydroquinone, 1,2-dihydroxybenzene (catechol) and 4-(*N*,*N*-dimethylamino)phenol respectively. These are supported by internal consistency of measured values of K_{37}. Their value of $E_{13.5}(A\cdot^-/A^{2-}) = 266$ mV for A^{2-} = *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine is similarly supported by other redox equilibria,[64] and by earlier electrochemical measurements[65] so that an estimate[8] of 88 mV may be discounted. All the equilibria were measured at $I \approx 0.5$. It is worth stressing again that values of reduction potentials enable the *thermodynamic feasibility* of reactions to be calculated, not the *likelihood*; deprotonation of reactants may be necessary before the *rates* of reaction become sufficiently fast for the reaction to proceed. The lack of reversibility of the NAD·/NADH couple for nicotinamide adenine dinucleotide has been discussed.[66]

6.5. Inorganic Indicators Other Than Oxygen

Reference to Table 9 indicates the high reliability of $E°(ClO_2\cdot/ClO_2^-) = 934$ mV. More powerful oxidants include halogen- and pseudohalogen radical-anions, e.g. $(SCN)_2\cdot^-$ or $Br_2\cdot^-$; the reduction potentials of these radicals are established to *ca.* ± 30 mV; values of $E°((SCN)_2\cdot^-/2SCN^-) = 1330$ mV and $E°(Br_2\cdot^-/2Br^-) = 1660$ mV are presently recommended.

A useful, very low potential inorganic oxidant is Tl^+, the reduced form of which is in equilibrium with Tl_2^+:

$$Tl^0 + Tl^+ \rightleftharpoons Tl_2^+. \qquad (38)$$

The equilibrium constant $K_{38} = 140$ dm^3 mol^{-1} and under certain conditions equilibrium *38* may be attained faster than electron transfer between Tl^+ and reductants.[67] Hence providing account is taken of the equilibrium *38*, the reduction potential of very low potential oxidants may be derived using Tl^+ as indicator and $E°(Tl^+/Tl_{aq}^0) = -1.94$ V.[67]

7. Prediction of Reduction Potentials for Unknown Couples

7.1. Use of Polarographic and Cyclic Voltammetric Data Obtained Using Non-Aqueous Solvents

The literature of electrochemical measurements of $E(A/A\cdot^-)$, $E(A\cdot^-/A^{2-})$ in aprotic solvents is voluminous. Such measurements will generally differ considerably in absolute terms (when corrected to s.h.e., see above, Sec. 2.2) from corresponding values for water. However, relative effects in aprotic solvents, e.g. the influence of substituents[68] in a molecule of known potential in aqueous solution, may be useful. Measurements in water using cyclic voltammetry correlate[69] but do not necessarily equate with the reversible potentials $E(A/A\cdot^-)$ (but see Sec. 3.4, above). The greatest discrepancies will be where molecules have substituents with prototropic functions.

7.2. Correlations Between Reduction Potentials and Rate Constants

There are several correlations of k_1, k_{-1} with ΔE_1 of the form based upon the Marcus theory (e.g. with radiation-produced radicals[64,70,71]). Values of $E(A/A\cdot^-)$, for example, may sometimes be estimated from other rate constants providing they are well below the diffusion-controlled limits. Values of k_7 were correlated with the e.s.r. characteristics (see below) of $A\cdot^-$ for A = nitrobenzenes,[72] and are therefore linked to reduction potentials.

7.8. Correlations Between Reduction Potential and Other Physico-Chemical Parameters

The correlations well established for polarographic potentials[66] provide a guide to other useful parameters which may be used to predict values for unknown couples. Hammett substituent constants (σ values) are the most useful, e.g. for 5-substitution of 1-methyl-2-nitroimidazole we have:[73]

$$E(\mathrm{A}/\mathrm{A}\cdot^-)/\mathrm{mV} = -(406 \pm 5) + (146 \pm 8)\sigma_p^- \quad . (74)$$

Hammett constants are well known to correlate with hyperfine splittings (h.f.s.) in the electron spin resonance spectra of radical-anions of series of derivatives and a useful correlation between the N (NO_2) h.f.s. and $E(\mathrm{A}/\mathrm{A}\cdot^-)$ has been made.[7] Variations between mono- and dinitrosubstituted series were noted.[74] Of course, relationships such as Eq. (74) will only be reliable predictors *either* when prototropic functions which could modulate E_m are absent, *or* when the pH is sufficiently high that E_m is unaffected by further increases in pH (all groups ionized or deprotonated). Since σ values are a measure of pK_a shifts, it would be theoretically possible to modify relationships between E_m and pH to incorporate σ as a predictor, but the relationships would be complex.

8. Arrangement of the Data Tables and Indexes

8.1. Content of the Tables

The Tables fall into 3 distinct groups. Tables 1 to 4 present reduction potentials of organic oxidants, in the form $E(\mathrm{A}/\mathrm{A}\cdot^-)$ where A is a stable ground state and $\mathrm{A}\cdot^-$ the radical produced on one-electron reduction. Tables 5 to 8 present reduction potentials of the radicals obtained upon one-electron oxidation of organic reductants, in the form $E(\mathrm{A}\cdot^-/\mathrm{A}^{2-})$ where A^{2-} represents a stable reductant and $\mathrm{A}\cdot^-$ the radical (disregarding prototropic state, of course). Table 9 presents reduction potentials of inorganic species, but without separation into groups where the radical is either reductant or oxidant.

The systematic names for many of the compounds are complex, and (except for inorganic couples) rather than arrange alphabetically, compounds in Tables 1 to 8 are subdivided into related groups. Within each group, compounds are generally listed in related sub-groups with increasing element count (C,H,N etc.) in substituents defining order where appropriate. With the structures at the foot of appropriate pages, the various groupings should be reasonably clear. Multiple entries for any one couple appear in order of publication year.

Each table contains 10 main columns: (*1*) A compound reference number. (*2*) The reduction potential of ground state or radical, as appropriate, all referring to one-electron reduction and all vs. the standard hydrogen electrode. These potentials are all mid-point potentials, E_m and in many, although not all cases, may be used as estimates for standard potentials, $E°$. Whether a measured or calculated value for E as tabulated equates or approximates to a standard potential depends largely upon the possible or known occurrence of prototropic equilibria involving either reductant, or oxidant, as discussed in Sec. 4. Column (*3*) gives the pH of measurement (or to which the calculation refers, where appropriate). Except where electrochemical methods were used most of the values were obtained by measurement of the concentrations of radicals and ground states at equilibrium, as outlined in Secs. 1 and 3. These have the symbol C (for concentrations) in column (*9*). A minority were determined from the kinetics of approach to equilibrium (Sec. 3.7). In this case K (for kinetics) appears in column (*9*). Either C or K may appear in parentheses where the data were secondary to, i.e. merely supported, the calculation of ΔE. Column (*4*) gives the reference compound used in the electron-transfer equilibrium, and (*5*) the reference potential *assumed* in the calculation of E (see below).

Since many values were derived from radiation-chemical experiments in which *either* one-electron oxidation *or* reduction was selected by using scavengers as described in Secs. 3.1, 3.2, in column (*6*) the co-solute (scavenger) is given, to help describe the experiment. As described in Sec. 3.8, ionic strength frequently influences measured equilibrium constants or kinetics, and column (*7*) gives an approximate ionic strength to which the experiments relate. The expression: →0 appears in column (*7*) if the experimental values were extrapolated to zero ionic strength. Column (*8*) notes the experimental method used: if only C and/or K appears, as described above, then the method involved monitoring fast electron-transfer equilibria following generation of radicals by pulse radiolysis, before the radical species disappear by other routes. The final column, (*10*) gives the reference number of the study, using the number assigned by the Radiation Chemistry Data Center of the University of Notre Dame and is common to the many publications of the Center and its online databases.

8.2. Alterations to Published Values

In general, only correction to s.h.e. (where appropriate) has been made to the original data. Where a value seems questionable, this is indicated by a dagger alongside the value, usually with an explanatory note in the Comments/method column. A recommended value is indicated by an asterisk. Many of the values may be immediately corrected by the reader using new recommendations or new values for reference potentials as they become available, since the Table indicates the reference couple and value assumed in the original work. Such corrections will be relatively minor and presentation of original data seemed preferable to making minor changes which will themselves by subject to revision as refinements to reference potentials are published.

8.3. Inorganic Couples: Standard States

The user is reminded that the standard state for a substance is that existing in its normal state at standard temperature and pressure (Sec. 2.2.), i.e. for gases such as oxygen it is 1 atmosphere partial pressure. For calculations of equilibrium constants where concentrations are appropriate, the Nernst equation should be used to calculate a reduction potential corresponding to unit concentration. More detailed discussion of numerous inorganic couples is given in Stanbury's recent compilation,[75] but the reader is warned that the latter author presents data uniformly using a standard state of 1 mol dm^{-3}, including couples involving gases.

9. Some Other Compilations of Reduction Potentials

Clark's classical text[22] includes compilations of many reduction potentials of organic substances. The volume by Bard et al.[11] supersedes an earlier compilation[10] of reduction potentials of inorganic substances in aqueous solution. Stanbury's review[75] discusses inorganic couples involving free radicals in more detail (note the comment about standard states in Sec. 8.3). Steenken[76] presents comprehensive information concerning electron transfer equilibria involving radicals and radical ions in aqueous solution. This includes values of reduction potentials as well as data characterizing the kinetics of electron-transfer equilibria involving radicals. Koppenol and Butler have discussed the energetics of interconversion of oxyradicals.[77]

10. List of Abbreviations and Symbols

A	General symbol for oxidant or electron acceptor
A*	Triplet excited state of species A
A^{2-}	General symbol for fully dissociated form of reductant AH_2
A_i	Absorbance of species *i*
a_A	Activity of species A
AcOH	Acetic acid
AH^{-}	General symbol for partially dissociated form of reductant AH_2
AH_2	General symbol for reductant or electron donor
Approx.	Approximate
AQS^{-}	9,10-Anthraquinone-2-sulfonate (Tables, 1.3.1)
Au.	This author (PW)
bpy	2,2′-Bipyridine
t-BuOH	*tert*-Butyl alcohol (2-Methylpropan-2-ol)
BV^{2+}	Benzyl viologen (1,1′-Dibenzyl-4,4′-bipyridinium) (Tables, 3.8.39)
C (in Methods column)	Concentrations used to estimate equilibrium constant (Introduction, Sec. 8.1)
CAT	Catechol (1,2-Dihydroxybenzene) (Tables, 5.2.1)
Calc.	Calculated
Calc. data	Calculated by the present author from data in reference shown
Calc. lit.	Calculated by the authors in the reference shown from literature data
Calcn.	Calculation
Consts.	Constants
Cyc. v.	Cyclic voltammetry
Diff. pulse volt.	Differential pulse voltammetry
DMAP	4-(Dimethylamino)phenol (Tables, 5.1.8)
DQ	Duroquinone (2,3,5,6-Tetramethyl-1,4-benzoquinone) (Tables 1.1.7)
E	General symbol for reduction potential
E°	Standard reduction potential (Introduction, Sec. 4.2)
E_0	Formal reduction potential (Introduction, Secs. 4.3, 4.4)
E_h	Reduction potential of half-cell relative to s.h.e. (Introduction, Sec. 4.2)
E_m	Mid-point potential of half-cell (Introduction, Sec. 4.3)
E_{mi}	Mid-point potential of half-cell at pH = *i* (Introduction, Sec. 4.4)
Eq.	Equation
Extrap.	Extrapolated
F	The Faraday constant = 9.649×10^4 C mol^{-1}
f_A	Activity coefficient of species A
$f(I)$	Ionic strength function (Introduction, Sec. 3.8)
Fp	Flash photolysis
Glycol	Ethylene glycol (1,2-Ethanediol)
GlyTyr	Glycyl-L-tyrosine
h	Planck's constant = 6.626×10^{-34} J s
HQ	Hydroquinone (1,4-Dihydroxybenzene) (Tables, 5.4.1)
I	Ionic strength
k	Rate constant
K	Equilibrium constant (expressed in terms of activities)
K'	Equilibrium constant (expressed in terms of concentrations)
K_a	Dissociation constant of an acid or the conjugate acid of a base
K_D	Equilibrium constant for dissociation of dimer (Introduction, Sec. 6.3)
K_f	Equilibrium constant of semiquinone formation equilibrium (Introduction, Sec. 5.1)

K_s	Apparent semiquinone formation constant at pH = 7 (Introduction, Sec. 5.2)
k (in Methods column)	Kinetics used to estimate equilibrium constant (Introduction, Sec. 8.1)
Kin.	Kinetics
MV^{2+}	Methyl viologen (1,1′-Dimethyl-4,4′-bipyridinium) (Tables, 3.8.2)
n	Number of electrons transferred in the oxidant/reductant couple
NAD^+	Nicotinamide-adenine dinucleotide (Tables, 4.4.6)
NADH	Nicotinamide-adenine dinucleotide, reduced form (Tables, 8.2.1)
n.c.e.	Normal calomel electrode (1 mol dm^{-3} KCl)
Pol.	Polarography
Pot.	Potentiometry
Potl.	Potential
2-PrOH	*iso*Propyl alcohol (Propan-2-ol)
Q	General symbol for quinones
QH_2	General symbol for hydroquinones
R	The gas constant = 8.314 J K^{-1} mol^{-1}
Rad.	Radiolysis
Rec.	Recommended
Reduct.	Reduction
Ref.	Reference
S_o	Sum of all oxidant species (Introduction, Sec. 4.3)
S_r	Sum of all reductant species (Introduction, Sec. 4.3)
s.c.e.	Saturated calomel electrode
Sec.	Section
s.h.e.	Standard (normal) hydrogen electrode
Spect.	Spectrophotometry
T	Absolute temperature
TMP	3,4,7,8-Tetramethylphenanthroline
TMPD	*N*,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine (Tables, 6.1.5)
TQ^{2+}	Triquat (7,8-Dihydro-6*H*-dipyrido[1,2-*a*:2′,1′-c] diazapinediium) (Tables, 3.4.1)
v/v	Parts by volume
z_A	Net charge (valency) on ion A
ν	Frequency
σ_p^-	Hammett sigma substituent constant (from *para* substituted phenols)
ΔE	Difference in reduction potentials (Introduction, Sec. 1)
ΔG	Free energy change accompanying reaction

11. Acknowledgments

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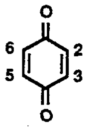
TABLE 1. Reduction potentials of quinones ($Q/Q^{\bullet -}$)

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
1.1.	**Benzoquinones (1a)**								
1.1.1	1,4-Benzoquinone	78 *	7					Rec. value; calc.; see Introduction (Sec. 5.4)	
		104	~7					Calc. from semiquinone formation consts. measured pH 6-7.	66C003
		99	7					Calcn.	761063
		399	0						
1.1.2	Methyl-1,4-benzoquinone	23	7					Calc. lit.	761063
1.1.3	2,3-Dimethyl-1,4-benzoquinone	−74	7					Calc. lit.	761063
1.1.4	2,5-Dimethyl-1,4-benzoquinone	−67	7					Calc. lit.	761063
		210	0						
1.1.5	2,6-Dimethyl-1,4-benzoquinone	−80	7					No details	765319
1.1.6	2,3,5-Trimethyl-1,4-benzoquinone	−165	7					Calc. lit.	761063
1.1.7	2,3,5,6-Tetramethyl-benzoquinone	−260 *	7					Rec. value; see Introduction (Sec. 6.2)	
		−250	7					Calc. lit.	74C001
		65	0					Calc. lit.	741141
		−235	7					Calc. lit.	751090
		−240	7					Calc. lit.	761063
		65	0						
		−244	7	BV^{2+}	−354	2-PrOH	→0	C (K)	761070
		−242	7	BV^{2+}	−355		→0	C; calc. data	80A349
		−247	7	BV^{2+}	−354	2-PrOH	→0	C	83C002
1.1.8	2,5-Diaziridinyl-3,6-bis(2-hydroxyethylamino)-1,4-benzoquinone (BZQ) (**1b**, $R^2 = R^5 = NHCH_2CH_2OH$)	−383	7	MV^{2+}	−450	HCO_2^-	0.12	C	87A269
		−370	7	3.8.31	−290	HCO_2^-	0.12	C	87A269
1.1.9	2,5-Diaziridinyl-3,6-bis(carbethoxyamino)-1,4-benzoquinone (AZQ) (**1b**, $R^2 = R^5 = NHCO_2Et$)	−168 †	7	DQ	−244	*t*-BuOH	~0.010	K	81C031
		−65	7	1.2.5	−110	HCO_2^-	0.12	C	87A269
		−70	7	1.1.4	−66	HCO_2^-	0.12	C	87A269
		−73	7	O_2 (1 mol dm^{-3})	−155	HCO_2^-	0.12	K	87A269



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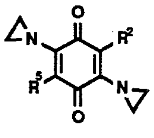
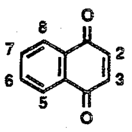


(1b)

TABLE 1. Reduction potentials of quinones ($Q/Q^{\cdot -}$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
1.2. Naphthoquinones									
1.2.1	1,2-Naphthoquinone	−89	7.8			HCO_2^-	0.11	C	86R230
1.2.2	1,4-Naphthoquinone (**1c**)	−140	7.8			HCO_2^-	0.11	C	86R230
1.2.3	5-Hydroxy-1,4-naphthoquinone (juglone)	−93	7	O_2 (1 mol dm^{-3})	−155	HCO_2^-	~0.1	C; data at other pH values, also with 1.1.5	87A234
1.2.4	5,8-Dihydroxy-1,4-naphthoquinone	−110	7	1.1.5	−80	HCO_2^-		C	83A039
		−103	5.5			HCO_2^-		C; other values pH 5.5-11	83A039
1.2.5	1,4-Naphthoquinone-2-sulfonate ion (**1d**, $R^2 = SO_3^-$)	−60	7	O_2 (1 atm.)	−330	HCO_2^-	0.1	C	761063
1.2.6	2-Methyl-1,4-naphthoquinone (**1d**, $R^2 = CH_3$)	−203	7	O_2 (1 atm.)	−325	HCO_2^-	~0.02	C	751090
		−206	7	DQ	−235	2-PrOH	~0.01	C; calc. data	751090
		−203	7.67	O_2 (1 mol dm^{-3})	−155	2-PrOH	<0.01	C	86B096
		−199	7.67	BV^{2+}	−354	2-PrOH	→0	C	86B096
1.2.7	(**1d**, $R^2 = CH_2OH$)	−152	7.67	O_2 (1 mol dm^{-3})	−155	2-PrOH	<0.01	C	86B096
1.2.8	(**1d**, $R^2 = CH_2OCH_3$)	−129	7.67	O_2 (1 mol dm^{-3})	−155	2-PrOH	<0.01	C	86B096 761063
1.2.9	(**1d**, $R^2 = CH_2OCOCH_3$)	−100	7.67	O_2 (1 mol dm^{-3})	−155	2-PrOH	<0.01	C	86B096
1.2.10	(**1d**, $R^2 = CH_2OCONHCH_2CH_2Cl$)	−122	7.67	O_2 (1 mol dm^{-3})	−155	2-PrOH	<0.01	C	86B096
1.2.11	(**1e**, $R^6 = CH_2Br$)	−92	7.67	O_2 (1 mol dm^{-3})	−155	2-PrOH	<0.01	C	86B096
1.2.12	(**1e**, $R^6 = CH_2Cl$)	−94	7.67	O_2 (1 mol dm^{-3})	−155	2-PrOH	<0.01	C	86B096
1.2.13	(**1e**, $R^6 = CH_2OCOCH_3$)	−94	7.67	O_2 (1 mol dm^{-3})	−155	2-PrOH	<0.01	C	86B096
1.2.14	(**1e**, $R^6 = CH_2OCONHCH_3$)	−99	7.67	O_2 (1 mol dm^{-3})	−155	2-PrOH	<0.01	C	86B096
1.2.15	2,3-Dimethyl-1,4-naphthoquinone (**1f**, $R^3 = CH_3$)	−240	7	O_2 (1 atm.)	−330	HCO_2^-	0.1	Calc. lit.	761063



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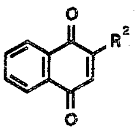

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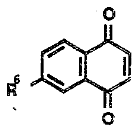

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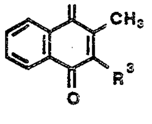

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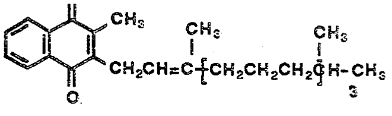
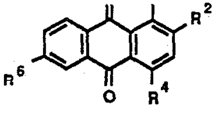


(1g)

TABLE 1. Reduction potentials of quinones ($Q/Q^{\cdot -}$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
1.2.	**Naphthoquinones**—Continued								
1.2.16	(**1f**, R^3 = S-glutathionyl)	−192	7.67	O_2 (1 mol dm^{-3})	−155	2-PrOH	<0.01	C	86B096
1.2.17	2-Methyl-3-phytyl-1,4-naphthoquinone (**1g**)	−170	7					Calc. lit.	761063
1.3.	**Anthraquinones**								
1.3.1	9,10-Anthraquinone-2-sulfonate ion (**1h**, $R^2 = SO_3^-$, $R^1 = R^4 = R^6 = H$)	−390 *						Rec. value; see Introduction (Sec. 6.2)	
		−380	7	DQ	−235	2-PrOH	~0.010	C	751117
		−375	7	BV^{2+}	−354	2-PrOH	→0	C	761070
		−377	7	DQ	−244	2-PrOH	→0	C; calc. data	761070
		−375	7	DQ	−244	2-PrOH	→0	C; calc. data	80A349
		−373	7	BV^{2+}	−355	2-PrOH	→0	C; calc. data	80A349
		−366	7	BV^{2+}	−354	2-PrOH	→0	C	83C002
		−381	7	TQ^{2+}	−548	2-PrOH	→0	C	83C002
1.3.2	1,4-Dihydroxy-9,10-anthraquinone-2-sulfonate ion (**1h**, $R^1 = R^4 = OH$, $R^2 = SO_3^-$, $R^6 = H$)	−270	7	3.3.1	−350	HCO_2^-	0.1	C; other data pH 6-11	88A901
1.3.3	1,4-Dihydroxy-9,10-anthraquinone-6-sulfonate ion (**1h**, $R^1 = R^4 = OH$, $R^2 = H$, $R^6 = SO_3^-$)	−249	7	3.3.1	−350	HCO_2^-	0.1	C; other data pH 7-11	88A901
1.3.4	1,4-Dihydroxy-5,8-bis[(2-hydroxyethylamino)-ethyl]amino-9,10-anthraquinone (**1i**, $R^1 = R^4 = OH$, $R^5 = R^8 = NHCH_2CH_2NHCH_2CH_2OH$)	−527	7					C; no details	87R257
1.3.5	1,4-Bis[(2-hydroxyethyl-amino)ethyl]amino-9,10-anthraquinone diacetate (**1i**, $R^1 = R^4 = NHCH_2CH_2NHCH_2CH_2OAc$, $R^5 = R^8 = H$)	−348	7	BV^{2+}	−354			K	81C031
1.4.	**Isoindole-4,7-diones**								
1.4.1	(**1j**, $R^1 = R^2 = CH_3$, $R^3 = C_6H_5$)	−440	7	AQS^-	−380	2-PrOH	~0.002	C	84R027
1.4.2	(**1j**, $R^1R^2 = -CH_2CH_2CH_2-$, $R^5(R^6) = CH_3$)	−420	7	AQS^-	−380	2-PrOH	~0.002	C; mixture of isomers.	84R027



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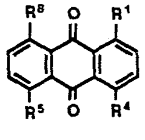

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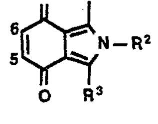
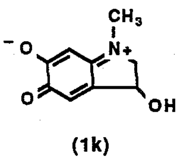


(1j)

TABLE 1. Reduction potentials of quinones ($Q/Q^{\bullet -}$)—Continued

No.	Compound or couple	*E*/mV	pH	Ref. compound	Ref. *E* /mV	Co-solute	*I*	Method/ comments	Ref.
1.4.	**Isoindole-4,7-diones**—Continued								
1.4.3	(**1j**, $R^1 = CH_3$, $R^2 = CH_3$, $R^3 = C_6H_5$, $R^5(R^6) = CH_3$)	−423	7	AQS^-	−380			C	82A329
1.4.4	(**1j**, $R^1 = C_6H_5$, $R^2R^3 = -CH_2CH_2CH_2-$)	−427	7	AQS^-	−380				
1.4.5	(**1j**, $R^2 = CH_3$, $R^3 = C_6H_5$)	−419	7	AQS^-	−380				
1.4.6	(**1j**, $R^1 = CH_3$, $R^2R^3 = -CH_2CH_2CH_2-$)	−438	7	AQS^-	−380				
1.4.7	(**1j**, $R^1R^2 = -CH_2CH_2CH_2-$, $R^3 = C_6H_5$, $R^5 = R^6 = CH_3$)	−435	7	AQS^-	−380	2-PrOH	~0.002	C	84R027
1.4.8	(**1j**, $R^1 = R^2 = R^5 = R^6 = CH_3$, $R^3 = C_6H_5$)	−452	7	AQS^-	−380	2-PrOH	~0.002	C	84R027
1.4.9	(**1j**, $R^1 = CO_2C_2H_5$, $R^2R^3 = -CH_2CH_2CH_2-$, $R^5(R^6) = CH_3$)	−368	7	AQS^-	−380	2-PrOH	~0.002	C; mixture of isomers.	84R027
1.4.10	(**1j**, $R^1 = CO_2C_2H_5$, $R^2 = R^5(R^6) = CH_3$, $R^3 = C_6H_5$)	−366	7	2.1.9	−437	2-PrOH	~0.002	C; mixture of isomers.	84R027
1.4.11	(**1j**, $R^1 = CO_2C_2H_5$, $R^2R^3 = -CH_2CH_2CH_2-$, $R^5(R^6) = CH_3$, $R^6(R^5) = OCH_3$)	−383	7	2.1.9	−437	2-PrOH	~0.002	C; mixture of isomers.	84R027
		−378	7	2.1.10	−352	2-PrOH	~0.002	C	84R027
1.5.	**Miscellaneous quinones**								
1.5.1	Adrenochrome (**1k**)	−253	7	BV^{2+}	−354			K	81C031
1.5.2	5-Aminophthalazine-1,4-dione (**1l**)	240	~10.6	O_2 (1 mol dm^{-3})	−155	HCO_3^-		Chemiluminescence; ± 20 mV.	84C026
1.5.3	9,10-Phenanthrenequinone (**1m**)	−124	7.8			HCO_2^-	0.11	C	86R230
1.5.4	Adriamycin (**1n**, R = $COCH_2OH$)	−292	7	DQ	−244			K. Eq. vs. O_2 mis-calc., inconsistent (see 83C018)	81C031
		−328	7	DQ	−240	HCO_2^-	0.1	C; other values, pH 6-12.	83C018
		−341 *	7	several		HCO_2^-	0.1	Rec.; C	88A901



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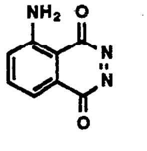

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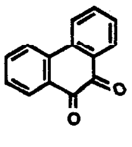

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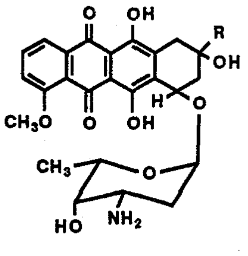

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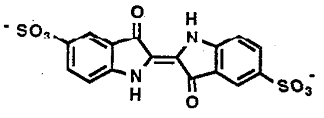
TABLE 1. Reduction potentials of quinones ($Q/Q^{\cdot -}$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
1.5.	**Miscellaneous quinones**—Continued								
1.5.5	Daunomycin (**1n**, R = $COCH_3$)	−305	7	DQ	−244			K	81C031
		−430 †	7	Q/QH_2	−410			Semiquinone formation const. + $E(Q/QH_2)$.	85A001
1.5.6	Indigodisulfonate ion (**1o**)	−247	7						59C002
1.5.7	Mitomycin C (**1p**)	−271	7	DQ	−244			K	81C031
		−238	7	BV^{2+}	−354			K	
		−310 *	7			HCO_2^-		Rec.; C	85R016
1.5.8	3,3',5,5'-Tetrabromodiphenoquinone (**1q**, X = Br)	260	7	BQ	99	CH_3CN (50% v/v)	~0.02	C (K), (fp)	81A405, 82B068
1.5.9	3,3',5,5'-Tetrachlorodiphenoquinone (**1q**, X = Cl)	260	7	BQ	99	CH_3CN (50% v/v)	~0.02	C (K), (fp)	81A405, 82B068
1.5.10	Methoxatine (**1r**)	−114	7.3	O_2 (1 mol dm^{-3})	−155	HCO_2^-	0.11	C + K	86A520
1.5.11	CI941 (**1s**)	−538	7.0	MV^{2+}		HCO_2^-	0.12	C	87R243
1.5.12	(**1t**, R = OCH_3)	(+)85	7.4	BQ	99	2-PrOH		C	88A125
		85	7.4	1.1.4	−66	N_3^-		C	88A125
1.5.13	(**1t**, R = $N(CH_3)_2$)	−10	7.4	BQ	99	2-PrOH		C	88A125
		−40	7.4	1.1.4	−66	2-PrOH		C	88A125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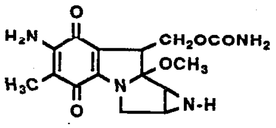
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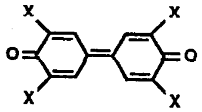
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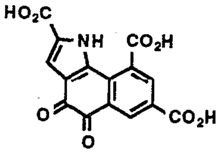
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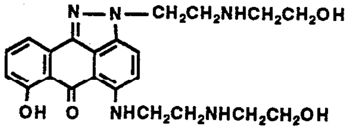
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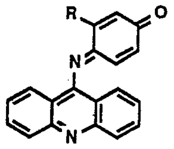
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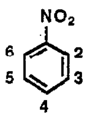
* Recomended value.

† Questionable or superseded value.

TABLE 2. Reduction potentials of nitroaryl compounds ($RNO_2/R\dot{N}O_2^-$)

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
2.1. Nitrobenzenes									
2.1.1	1,2-Dinitrobenzene	−287	7	DQ	−235	2-PrOH		C(K)	761111
2.1.2	1,3-Dinitrobenzene	−345	7	DQ	−235	2-PrOH		C(K)	761111
2.1.3	1,4-Dinitrobenzene	−257	7	DQ	−235	2-PrOH		C(K)	761111
2.1.4	2,4-Dinitrobenzoic acid	−345	7	DQ	−235	2-PrOH		C(K)	761111
2.1.5	2,5-Dinitrobenzoic acid	−272	7	DQ	−235	2-PrOH		C	761111
2.1.6	3,4-Dinitrobenzoic acid	−271	7	DQ	−235	2-PrOH		C	761111
2.1.7	3,5-Dinitrobenzoic acid	−344	7	DQ	−235	2-PrOH		C(K)	761111
2.1.8	2,4-Dinitrophenol	−500	7			2-PrOH	→0	C	82R118
2.1.9	3-Nitroacetophenone	−437	7	AQS^-	−380	2-PrOH	~0.010	C	751117
2.1.10	4-Nitroacetophenone	−358	7	DQ	−235	2-PrOH	~0.010	C	751117
		−353	7	AQS^-	−380	2-PrOH	~0.010	C	751117
2.1.11	Nitrobenzene	−486	7	AQS^-	−380	2-PrOH	~0.010	C	751117
		−486	7	AQS^-	−375	*t*-BuOH	→0	C	80C024
2.1.12	2-Nitrobenzaldehyde	−355	7	DQ	−244	*t*-BuOH	→0	C	80C024
2.1.13	4-Nitrobenzaldehyde	−322	7	DQ	−244	*t*-BuOH	→0	C	80C024
2.1.14	2-Nitrobenzoic acid	−412	7	DQ	−235	2-PrOH		C(K)	761111
2.1.15	3-Nitrobenzoic acid	−433	7	DQ	−235	2-PrOH		C(K)	761111
2.1.16	4-Nitrobenzoic acid	−396	7	DQ	−235	2-PrOH		C(K)	761111
		−425	7	AQS^-	−375	2-PrOH	→0	C	80R182
2.1.17	2-Nitrobenzonitrile	−308	7	DQ	−244	*t*-BuOH	→0	C	80C024
2.1.18	4-Nitrobenzyl alcohol	−477	7						79R017
		−469	7	AQS^-	−375	2-PrOH	→0	C	79R017
		−487	7	MV^{2+}	−447	2-PrOH	→0	C	79R017
2.1.19	4-Nitro-(3′-dimethylamino)-propiophenone (**2a**, R^4 = $CO(CH_2)_2N(CH_3)_2$)	−315	7	AQS^-	−375	2-PrOH	→0	C	761037
2.1.20	(**2b**, R^6 = $CONH_2$)	−385	7						87R083
2.1.21	(**2b**, R^6 = $CONHCH_3$)	−387	7						87R083
2.1.22	(**2b**, R^6 = $CON(CH_3)_2$)	−377	7						87R083
2.1.23	(**2b**, R^6 = $CONHCH_2CH(OCH_3)_2$)	−384	7						87R083
2.1.24	(**2c**, R^4 = NH_2)	−460	7						87R083
2.1.25	(**2c**, R^4 = $N(CH_3)_2$)	−464	7						87R083
2.1.26	(**2d**, R^4 = $CONH_2$, R^6 = -N-aziridinyl)	−515	7						87R083
2.1.27	(**2d**, R^4 = -N-aziridinyl, R^6 = H_2)	−431	7						87R083



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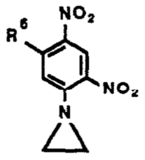

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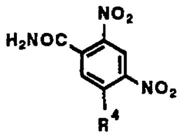

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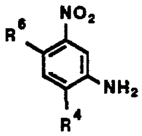

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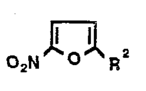
TABLE 2. Reduction potentials of nitroaryl compounds ($RNO_2/R\dot{N}O_2^-$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
2.2.	**Nitrofurans**								
2.2.1	5-Nitro-2-furoic acid (**2e**, $R^2 = CO_2H$)	−317	7	DQ	−235	2-PrOH	~0.010	C	751117
2.2.2	Nifuroxime (**2e**, $R^2 = CH{=}NOH$ (*anti*))	−253	7	DQ	−235	2-PrOH	~0.010	C	751117
2.2.3	2-Methoxymethyl-5-nitrofuran (**2e**, $R^2 = CH_2OCH_3$)	−338	7	BV^{2+}	−354	2-PrOH	$\to 0$	C	79R017
2.2.4	Nitrofurazone (**2e**, $R^2 = CH{=}NNHCONH_2$)	−257	7	BV^{2+}	−354	2-PrOH	$\to 0$	C	761037
2.2.5	Nitrofurantoin (**2e**, R^2 = **2f**)	−264	7	BV^{2+}	−354	2-PrOH	$\to 0$	C	80R185
2.2.6	Nifurpipone (**2e**, R^2 = **2g**)	−214	7	BV^{2+}	−354	2-PrOH	$\to 0$	C	761037
2.2.7	(**2e**, R^2 = -CH=CH-(2-quinolyl))	−276 −263	7 7	DQ 1.2.6	−245 −203	2-PrOH (50% v/v)	~0.10	K (fp)	79C021
2.2.8	(**2e**, R^2 = -CH=CH-CH=CH-(2-quinolyl))	−265 −256	7 7	DQ 1.2.6	−245 −203	2-PrOH (50% v/v)	~0.10	K (fp)	79C021
2.2.9	(**2e**, R^2 = -CH=C($CONH_2$)(2-furyl) = *cis*-AF-2)	−242	7	BV^{2+}	−354	2-PrOH	$\to 0$	C	84A208
2.2.10	(**2e**, R^2 = -CH=C($CONH_2$)(2-furyl) = *trans*-AF-2)	−276	7	BV^{2+}	−354	2-PrOH	$\to 0$	C	84A208
2.2.11	*N*-Butyl-5-nitro-2-furamide (**2e**, $R^2 = CONHnC_4H_9$)	−230	7	BV^{2+}	−354	2-PrOH	$\to 0$	C	84A263
2.3.	**2-Nitroimidazoles**								
2.3.1	2-Nitroimidazole (**2h**, R^4 = H)	−418 −508	7 9.2	AQS^-	−375	2-PrOH	$\to 0$	C	761070
2.3.2	2,4-Dinitroimidazole (**2h**, $R^4 = NO_2$ (4/5-nitro))	−445 −305 −265	6.93 4.1 3.26	BV^{2+} BV^{2+} BV^{2+}	−354 −354 −354	2-PrOH 2-PrOH 2-PrOH	$\to 0$ ~0.005 ~0.002	C	79R037
2.3.3	5-Cyano-1-methyl-2-nitroimidazole (**2i**, R^5 = CN)	−267	7	DQ	−244	2-PrOH	$\to 0$	C	80R187
2.3.4	1-Methyl-2-nitroimidazole-5-carboxaldehyde (**2i**, R^5 = CHO)	−243	7	DQ	−244	2-PrOH	$\to 0$	C	761070
2.3.5	1-Methyl-2-nitroimidazole-5-carboxylate ion (**2i**, $R^5 = CO_2^-$)	−385	7	AQS^-	−375	2-PrOH	$\to 0$	C	773087
2.3.6	1-Methyl-2-nitroimidazole-5-carboxamide (**2i**, $R^5 = CONH_2$)	−321	7	AQS^-	−375	2-PrOH	$\to 0$	C	80R187
2.3.7	(**2i**, $R^5 = CH_2OH$)	−400	7	AQS^-	−375	2-PrOH	$\to 0$	C	79R017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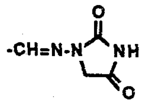
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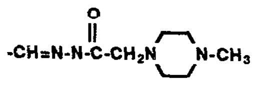
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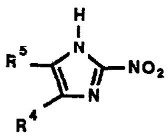
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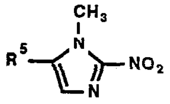
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TABLE 2. Reduction potentials of nitroaryl compounds ($RNO_2/R\dot{N}O_2^-$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
2.3.	**2-Nitroimidazoles**—Continued								
2.3.8	5-Ethenyl-1-methyl-2-nitroimidazole (**2i**, $R^5 = CH{=}CH_2$)	−392	7 7	AQS^-	−375	2-PrOH	→0	C	79R017
		−398	7	BV^{2+}	−354	2-PrOH	→0	C	85R035
2.3.9	(**2i**, $R^5 = CO_2CH_3$)	−300	7	DQ	−244	2-PrOH	→0	C	79R017
2.3.10	(**2i**, $R^5 = CH{=}N^+(\text{-}O^-)CH_3$)	−282	7	BV^{2+}	−354	2-PrOH	→0	C	79R017
2.3.11	(**2i**, $R^5 = CH(OH)CH_2OH$)	−396	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.12	(**2i**, $R^5 = CH(CH_3)_2$)	−439	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.13	(**2i**, $R^5 = C(CH_3)_2(OH)$)	−412	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.14	(**2i**, $R^5 = CH{=}N\text{-}N(CH_3)_2$)	−386	7	BV^{2+}	−354	2-PrOH	→0	C	80R184
2.3.15	(**2i**, $R^5 = CH{=}C(CN)_2$)	−240	7	BV^{2+}	−354	2-PrOH	→0	C	80R184
2.3.16	(**2i**, $R^5 = CH(OCOCH_3)_2$)	−350	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.17	(**2i**, $R^5 = CH{=}N\text{-}(N\text{-}morpholino)$)	−366	7	AQS^-	−375	2-PrOH	→0	C	80R184
2.3.18	(**2i**, $R^5 = CH{=}N\text{-}(N\text{-}piperazino)$)	−354	7	AQS^-	−375	2-PrOH	→0	C	80R184
2.3.19	(**2i**, $R^5 = CH{=}N\text{-}(N\text{-}piperidino)$)	−376	7	AQS^-	−375	2-PrOH	→0	C	80R184
2.3.20	2-Nitroimidazole-1-acetic acid (**2j**, $R^1 = CH_2CO_2H$)	−447	7	AQS^-	−375	2-PrOH	→0	C	80R185
2.3.21	1-(2-Hydroxyethyl)-2-nitroimidazole (**2j**, $R^1 = CH_2CH_2OH$)	−398	7	AQS^-	−375	2-PrOH	→0	C	761070
2.3.22	(**2j**, $R^1 = CH_2CH_2OH$, $R^4 = NO_2$)	−238	7	BV^{2+}	−354	2-PrOH	→0	C	79R037
2.3.23	1-(2-Hydroxyethyl)-5-methyl-2-nitroimidazole (**2j**, $R^1 = CH_2CH_2OH$, $R^5 = CH_3$)	−423	7	AQS^-	−375	2-PrOH	→0	C	761070
2.3.24	2-Nitro-1-(2-oxopropyl)imidazole (**2j**, $R^1 = CH_2COCH_3$)	−358	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.25	(**2j**, $R^1 = CH_2CO_2CH_3$)	−355	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.26	(**2j**, $R^1 = CH_2CH(OH)CH_2Cl$)	−384	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.27	(**2j**, $R^1 = CH_2CH(OH)CH_2F$)	−383	7	AQS^-	−375	2-PrOH	→0	C	79R017

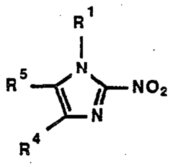

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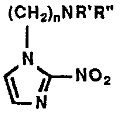
Table 2. Reduction potentials of nitroaryl compounds ($RNO_2/R\dot{N}O_2^-$)—Continued

No.	Nitrocompound or sample	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
2.3.	**2-Nitroimidazoles**—Continued								
2.3.28	1-(2-Methoxyethyl)-2-nitroimidazole (**2j**, $R^1 = CH_2CH_2OCH_3$)	−393	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.29	(**2j**, $R^1 = CH_2CH(OH)CH_2OH$)	−389	7	AQS^-	−375	2-PrOH	→0	C	761070
2.3.30	(**2j**, $R^1 = CH_2CH_2SO_2CH_3$)	−368	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.31	(**2j**, $R^1 = CH_2CH_2OCOCH_3$)	−420	7	AQS^-	−375	2-PrOH	→0	C	761070
2.3.32	(**2j**, $R^1 = CH_2CONHCH_2CH_2OH$)	−388						C	80R193
2.3.33	(**2j**, $R^1 = CH_2CO_2C_2H_5$, $R^5 = C_2H_5$)	−388	7	AQS^-	−375	2-PrOH	→0	C	761070
2.3.34	1-(2-Ethoxyethyl)-2-nitroimidazole (**2j**, $R^1 = CH_2CH_2OC_2H_5$)	−400	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.35	Misonidazole (**2j**, $R^1 = CH_2CH(OH)CH_2OCH_3$)	−389 *						Rec.	
		−363	7	DQ	−235	2-PrOH	~0.010	C	751117
		−398	7	AQS^-	−380	2-PrOH	~0.010	C	751117
		−389	7	AQS^-	−375	2-PrOH	→0	C	761070
		−389	7	AQS^-	−375	*t*-BuOH	→0	C (K)	761070
		−389	7	AQS^-	−375	HCO_2^-	→0	C, calc. data	761070
		−388	7	BV^{2+}	−354	2-PrOH	→0	C (K)	761070
2.3.36	1-[(2-Ethylsulfonyl)ethyl]-2-nitroimidazole (**2j**, $R^1 = CH_2CH_2SO_2C_2H_5$)	−368	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.37	(**2j**, $R^1 = CH_2CONHCH_2CHOHCH_2OH$)	−392						C	80R193
2.3.38	(**2j**, $R^1 = CH_2CH(OH)CH_2OCH_2CH{=}CH_2$)	−391	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.39	(**2j**, $R^1 = CH_2CON(CH_2CH_2OH)_2$)	−398						C	80R193
2.3.40	(**2j**, $R^1 = CH_2CH_2OC_6H_5$)	−391	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.41	(**2j**, $R^1 = CH_2CH_2SO_2C_6H_5$)	−367	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.42	Benznidazole (**2j**, $R^1 = CH_2CONHCH_2C_6H_5$)	−380	7	AQS^-	−375	2-PrOH	→0	C	761070
2.3.43	(**2j**, $R^1 = (CH_2)_3OC_6H_5$)	−409	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.44	(**2j**, $R^1 = CH_2CHOHCH_2O\text{-}CH(CH_2Cl)CH_2OCHMe_2$)	−395	7	AQS^-	−375	2-PrOH	→0	C	82R117
2.3.45	(**2k**, n = 2, NR′R″ = *N*-morpholino)	−390	7	AQS^-	−375	2-PrOH	→0	C	79R017
2.3.46	(**2k**, n = 2, NR′R″ = *N*-morpholino methiodide)	−318	7	AQS^-	−375	2-PrOH	→0	C	80R184
2.3.47	(**2k**, n = 3, NR′R″ = *N*-morpholino)	−386	7	AQS^-	−375	2-PrOH	→0	C	80R184

TABLE 2. Reduction potentials of nitroaryl compounds ($RNO_2/R\dot{N}O_2^-$)—Continued

No.	Compound or couple	*E*/mV	pH	Ref. compound	Ref. *E* /mV	Co-solute	*I*	Method/ comments	Ref.
2.3. 2-Nitroimidazoles—Continued									
2.3.48	(**2k**, n = 4, NR'R'' = *N*-morpholino)	−396	7	MV^{2+}	−447	2-PrOH	→0	C	80R184
2.3.49	(**2k**, n = 4, NR'R'' = *N*-morpholino methiodide)	−379	7	MV^{2+}	−447	2-PrOH	→0	C	80R184
2.3.50	(**2k**, n = 5, NR'R'' = *N*-morpholino)	−399	7	MV^{2+}	−447	2-PrOH	→0	C	80R184
2.3.51	(**2k**, n = 6, NR'R'' = *N*-morpholino)	−379	7	MV^{2+}	−447	2-PrOH	→0	C	80R184
2.3.52	(**2k**, n = 8, NR'R'' = *N*-morpholino)	−388	7	MV^{2+}	−447	2-PrOH	→0	C	80R184
2.3.53	(**2k**, n = 11, NR'R'' = *N*-morpholino)	−403	7	MV^{2+}	−447	2-PrOH	→0	C	80R184
2.3.54	(**2k**, n = 2, NR'R'' = *N*-pyrrolidino)	−334	7	AQS^-	−375	2-PrOH	→0	C	80R184
2.3.55	(**2k**, n = 4, NR'R'' = *N*-pyrrolidino)	−389	7	MV^{2+}	−447	2-PrOH	→0	C	80R184
2.3.56	(**2k**, n = 2, NR'R'' = *N*-piperidino)	−325	7	AQS^-	−375	2-PrOH	→0	C	80R184
		−316 −345	6 8						82Z198
2.3.57	(**2k**, n = 3, NR'R'' = *N*-piperidino)	−353	7	AQS^-	−375	2-PrOH	→0	C	80R184
2.3.58	(**2k**, n = 4, NR'R'' = *N*-piperidino)	−386	7	MV^{2+}	−447	2-PrOH	→0	C	80R184
2.3.59	(**2k**, n = 6, NR'R'' = *N*-piperidino)	−399	7	MV^{2+}	−447	2-PrOH	→0	C	80R184
2.3.60	(**2k**, n = 2, NR'R'' = 2-pyridyl)	−395	7	AQS^-	−375	2-PrOH	→0	C	80R184
2.3.61	(**2k**, n = 2, NR'R'' = *N*-anilino)	−398	7	AQS^-	−375	2-PrOH	→0	C	80R184
2.3.62	(**2k**, n = 2, NR'R'' = $N(CH(CH_3)_2)_2$)	−272	7	AQS^-	−375	2-PrOH	→0	C	80R184
2.3.63	(**2l**, NR'R'' = *N*-aziridino)	−398	7					C	84R149
2.3.64	(**2l**, NR'R'' = $N(CH_3)_2$)	−351	7	AQS^-	−375	2-PrOH	→0	C	80R186
2.3.65	(**2l**, NR'R'' = $N(C_2H_5)_2$)	−349	7	AQS^-	−375	2-PrOH	→0	C	80R186
2.3.66	(**2l**, NR'R'' = $N(CH_2CH_2OH)_2$)	−369	7	AQS^-	−375	2-PrOH	→0	C	80R186
2.3.67	(**2l**, NR'R'' = $NHC(CH_3)_3$)	−348	7	AQS^-	−375	2-PrOH	→0	C	80R186
2.3.68	(**2l**, NR'R'' = $NHCH_2C_6H_5$)	−353	7	AQS^-	−375	2-PrOH	→0	C	80R186
2.3.69	(**2l**, NR'R'' = $NHC_6H_4OCH_3(p)$)	−391	7	AQS^-	−375	2-PrOH	→0	C	80R186



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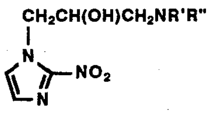

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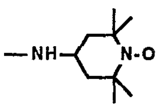
TABLE 2. Reduction potentials of nitroaryl compounds ($RNO_2/R\dot{N}O_2^-$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
2.3. 2-Nitroimidazoles—Continued									
2.3.70	(**2l**, NR′R″ = $NHCH_2C_6H_4OCH_3(p)$)	−350	7	AQS^-	−375	2-PrOH	→0	C	80R186
2.3.71	(**2l**, NR′R″ = **2m**)	−355	7	AQS^-	−375	2-PrOH	→0	C	80R186
2.3.72	(**2l**, NR′R″ = **2n**)	−361	7	AQS^-	−375	2-PrOH	→0	C	80R186
2.3.73	1-(3-*N*-Pyrrolidinyl-2-hydroxypropyl)-2-nitroimidazole (**2o**, X = absent)	−352	7	AQS^-	−375	2-PrOH	→0	C	80R186
2.3.74	(**2o**, X = CH_2)	−346	7	AQS^-	−375	2-PrOH	→0	C	80R186
2.3.75	(**2o**, X = CH_2, R″ = OH)	−357	7	AQS^-	−375	2-PrOH	→0	C	80R186
2.3.76	1-[3-(4-Morpholino)-2-hydroxypropyl]-2-nitroimidazole (**2o**, X = O)	−380	7	AQS^-	−375	2-PrOH	→0	C	80R186
2.3.77	(**2o**, X = NCH_3)	−370	7	AQS^-	−375	2-PrOH	→0	C	80R186
2.4. 4-Nitroimidazoles									
2.4.1	4-Nitroimidazole (**2p**, $R^2 = R^5 = H$)	≤-527	7	AQS^-	−375	*t*-BuOH	→0	C	761070
2.4.2	5-Iodo-4-nitroimidazole (**2p**, $R^2 = H$, $R^5 = I$)	−503	7	AQS^-	−380	2-PrOH	~0.010	C (K)	85A303
2.4.3	2-Methyl-4-nitroimidazole (**2q**, $R^2 = CH_3$)	−542	7	AQS^-	−380	2-PrOH	~0.010	C	751117
		−492	7	AQS^-	−375	*t*-BuOH	→0	C	771044
2.4.4	5-Bromo-1-methyl-4-nitroimidazole (**2q**, R^5 = Br)	−523	7	MV^{2+}	−447	2-PrOH	→0	C	82A033
2.4.5	5-Chloro-1-methyl-4-nitroimidazole (**2q**, R^5 = Cl)	~-517	7	AQS^-	−375	*t*-BuOH	→0	C	761070
		−534	7	MV^{2+}	−447	*t*-BuOH	→0	C	80A136
2.4.6	5-Iodo-1-methyl-4-nitroimidazole (**2q**, R^5 = I)	−529	7	MV^{2+}	−447	2-PrOH	→0	C	82A033
		−505	7	AQS^-	−380			C	85A303
2.4.7	5-Mercapto-1-methyl-4-nitroimidazole (**2q**, R^5 = SH)	−538	7		−486	2-PrOH	→0	C	80R183
2.4.8	1-Methyl-4-nitroimidazole-5-sulfonamide (**2q**, $R^5 = SO_2NH_2$)	−395	7	MV^{2+}	−447	2-PrOH	→0	C	80R183
2.4.9	(**2q**, $R^5 = SO_2CH_3$)	−355	7						81R072
2.4.10	(**2q**, $R^5 = SCH_2CO_2H$)	−545	7	MV^{2+}	−447	2-PrOH	→0	C	80R183
2.4.11	(**2q**, $R^5 = SO_2N(CH_3)_2$)	−409	7	MV^{2+}	−447	2-PrOH	→0	C	80R183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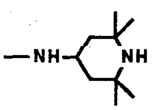
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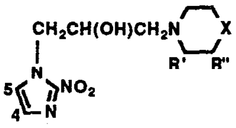
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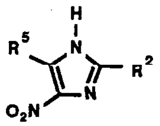
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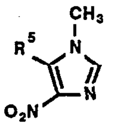
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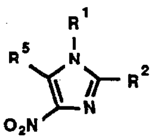
TABLE 2. Reduction potentials of nitroaryl compounds ($RNO_2/R\dot{N}O_2^-$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
2.4. 4-Nitroimidazoles—Continued									
2.4.12	(**2q**, R^5 = $SO_2NHCOCH_3$)	−523	7					C	81R072
2.4.13	(**2q**, R^5 = $SO_2NHCH_2N(CH_3)_2$)	−402	7					C	81R072
2.4.14	(**2q**, R^5 = SO_2-(*N*-morpholino))	−406	7					C	81R072
2.4.15	(**2q**, R^5 = SO_2NHCH_2-(*N*-morpholino))	−394	7	MV^{2+}	−447	2-PrOH	→0	C	80R183
2.4.16	(**2q**, R^5 = OC_6H_5)	−560	7					C	84R150
2.4.17	(**2q**, R^5 = *O*-(*p*-hydroxyphenyl))	−565	7					C	84R150
2.4.18	1-Methyl-5-phenylsulfonyl-4-nitroimidazole (**2q**, R^5 = $SO_2C_6H_5$)	−376	7					C	81R072
2.4.19	1-Methyl-5-phenoxysulfonyl-4-nitroimidazole (**2q**, R^5 = $SO_2OC_6H_5$)	−342	7	MV^{2+}	−447	2-PrOH	→0	C	80R183
2.4.20	1-Methyl-5-(4-chlorophenoxy)sulfonyl-4-nitroimidazole (**2q**, R^5 = SO_2O-(4-chlorophenyl))	−345	7	MV^{2+}	−447	2-PrOH	→0	C	80R183
2.4.21	1-Methyl-5-(4-nitrophenoxy)sulfonyl-4-nitroimidazole (**2q**, R^5 = SO_2O-(4-nitrophenyl))	−302	7					C	81R072
2.4.22	1-Methyl-5-phenylaminosulfonyl-4-nitroimidazole (**2q**, R^5 = $SO_2NHC_6H_5$)	−398	7	MV^{2+}	−447	2-PrOH	→0	C	80R183
2.4.23	1-Methyl-5-(2-chlorophenyl)aminosulfonyl-4-nitroimidazole (**2q**, R^5 = SO_2NH-(2-chlorophenyl))	−444	7					C	81R072
2.4.24	1-Methyl-5-(2-methylphenyl)aminosulfonyl-4-nitroimidazole (**2q**, R^5 = SO_2NH-(2-tolyl))	−426	7					C	81R072
2.4.25	(**2q**, R^5 = SO_2O-(2-methoxyphenyl))	−365	7					C	81R072
2.4.26	(**2q**, R^5 = SO_2O-(4-methoxyphenyl))	−335	7					C	81R072
2.4.27	(**2q**, R^5 = SO_2NH-(2-methoxyphenyl))	−408	7					C	81R072
2.4.28	(**2q**, R^5 = S-1'-(3-aminopurine))	−490	7	MV^{2+}	−447	2-PrOH	→0	C	80R183
2.4.29	(**2q**, R^5 = S-1'-(3-amino-6-(2-methylpropyl)purine))	−503	7	TQ^{2+}	−548	2-PrOH	→0	C	80R183
2.4.30	(**2q**, R^5 = SO_2O-(1-naphthyl))	−340	7					C	81R072
2.4.31	(**2q**, R^5 = SO_2NH-(1-naphthyl))	−453	7					C	81R072

TABLE 2. Reduction potentials of nitroaryl compounds ($RNO_2/R\dot{N}O_2^-$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
2.4. 4-Nitroimidazoles—Continued									
2.4.32	(**2r**, $R^1 = CH_3$, $R^2 =$ Br)	−515	7					C	84R150
2.4.33	2-Iodo-1-methyl-4-nitroimidazole (**2r**, $R^1 = CH_3$, $R^2 =$ I)	−521	7	MV^{2+}	−447	2-PrOH	→0	C	82A033
2.4.34	(**2r**, $R^1 = CH_3$, $R^2 = NO_2$)	−243	7					C	84R150
2.4.35	(**2r**, $R^1 = CH_3$, $R^2 = SO_2CH_3$)	−446	7					C	84R150
2.4.36	(**2r**, $R^1 = CH_2CH(OH)CH_2OH$, $R^5 =$ I)	−512	7						84R150
2.4.37	(**2r**, $R^1 = CH_2CO_2C_2H_5$, $R^5 =$ I)	−436	7	AQS^-	−480			C (K)	85A303
2.4.38	(**2r**, $R^1 = CH_2CH(OH)CH_2OCH_3$, $R^5 =$ I)	−497	7	AQS^-	−480			C	85A303
2.4.39	(**2r**, $R^1 = CH_2CH(OH)CH_2OCH_3$, $R^2 = CH_3$)	−564	7	MV^{2+}	−447		→0	C	79R017
		−583	7	TQ^{2+}	−548		→0	C	80C008
2.4.40	(**2r**, $R^1 = CH_2CH_2$-(*N*-morpholino))	−554	7	MV^{2+}	−554		→0	C	79R017
2.4.41	(**2r**, $R^1 = CH_2CONHCH_2$-(3-pyridyl-*N*-oxide), $R^5 =$ I)	−465	7	AQS^-	−380			C	85A303
2.4.42	(**2s**)	−439	7	AQS^-	−375		→0	C	771044
2.4.43	(**2t**)	−335	7					C	84R150
2.4.44	(**2q**, $R^5 = SC_6H_5$)	−501	7						84R150
2.5. 5-Nitroimidazoles									
2.5.1	4-Bromo-1-methyl-5-nitroimidazole (**2u**, $R^4 =$ Br)	−460	7	MV^{2+}	−447	2-PrOH	→0	C	82A033
2.5.2	4-Iodo-1-methyl-5-nitroimidazole (**2u**, $R^4 =$ I)	−461	7	MV^{2+}	−447	2-PrOH	→0	C(K)	82A033
		−464	7	AQS^-	−380			C	85A303
2.5.3	(**2u**, $R^4 = SO_2$-(*N*-morpholino))	−334	7					C	83R015
2.5.4	(**2u**, $R^4 = SO_2NH_2$)	−336	7					C	83R015
2.5.5	(**2u**, $R^4 = SO_2C_6H_5$)	−324	7					C	83R015
2.5.6	(**2u**, $R^4 = SO_2OC_6H_5$)	−259	7					C	83R015



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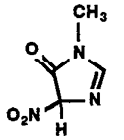

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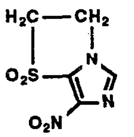

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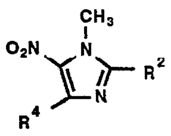

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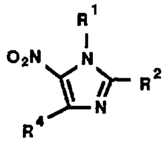
TABLE 2. Reduction potentials of nitroaryl compounds ($RNO_2/R\dot{N}O_2^-$)—Continued

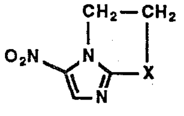
No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
2.5.	**5-Nitroimidazoles**—Continued								
2.5.7	2-Iodo-1-methyl-5-nitroimidazole (**2u**, $R^2 = I$)	−454	7	MV^{2+}	−447	2-PrOH	→0	C	82A033
2.5.8	(**2u**, $R^2 = NO_2$)	−178	7					C	84R150
2.5.9	1-Methyl-5-nitroimidazole-2-carboxaldehyde (**2u**, $R^2 = CHO$)	−360	7	AQS^-	−375	2-PrOH	→0	C	82R117
		−360	7	BV^{2+}	−354	2-PrOH	→0	C	82R117
2.5.10	1,2-Dimethyl-5-nitroimidazole (**2u**, $R^2 = CH_3$)	−475	7	AQS^-	−375	2-PrOH	→0	C	761070
		−480	7	AQS^-	−375	HCO_2^-	→0	C, calc. data	761070
2.5.11	(**2u**, $R^2 = SOCH_3$)	−361	7					C	84R150
2.5.12	(**2u**, $R^2 = SO_2CH_3$)	−351	7					C	84R150
2.5.13	(**2u**, $R^2 = S(CH_2)_2O$-(4-carboxyphenyl))	−481	7	MV^{2+}	−447	2-PrOH	→0	C	85R035
2.5.14	(**2v**, $R^1 = CH_2CH_2OPO_3^{2-}$, $R^2 = CH_3$, Na_2salt (?))	−509	7	AQS^-	−375	*t*-BuOH	→0	C	771044
2.5.15	(**2v**, $R^1 = CH_2CH_2OH$, $R^2 = CH_3$)	−486 *	7					Rec.	
		−485	7	AQS^-	−375	2-PrOH	→0	C, calc. data	761070
		−488	7	AQS^-	−375	*t*-BuOH	→0	C (K), calc. data	761070
		−486	7	AQS^-	−375	*t*-BuOH	→0	C	771044
		−451	7	3.8.10	−410	*t*-BuOH		C	85A090
		−476	7	AQS^-	−380	*t*-BuOH		C	85A090
2.5.16	(**2v**, $R^1 = CH_2CH(OH)CH_2Cl$, $R^2 = CH_3$)	−467 *	7	AQS^-	−375	2-PrOH	→0	Rec.; C	761070
		−474	7	AQS^-	−375	HCO_2^-	→0	C, calc. data	761070
2.5.17	(**2v**, $R^1 = CH_2CO_2C_2H_5$, $R^4 = I$)	−475	7	AQS^-	−375			C	85A303
2.5.18	(**2v**, $R^1 = CH_2CH(OH)CH_2OCH_3$, $R^4 = I$)	−441	7	AQS^-	−375			C	85A303
2.5.19	(**2v**, $R^1 = CH_2CH_2NHC(=S)OCH_3$, $R^2 = CH_3$)	−498	7	MV^{2+}	−447		→0	C	79R017
2.5.20	(**2v**, $R^1 = CH_2CH(OH)CH_2OCH_3$, $R^2 = CH_3$)	−479 *	7	AQS^-	−375	2-PrOH	→0	Rec.; C	761070
		−475	7	AQS^-	−375	HCO_2^-	→0	C	761070
2.5.21	1-(2-Ethylsulfonyl)-ethyl-2-methyl-5-nitroimidazole (**2v**, $R^1 = CH_2CH_2SO_2C_2H_5$, $R^2 = CH_3$)	−464	7	AQS^-	−375	*t*-BuOH	→0	C	761070



(2v)

TABLE 2. Reduction potentials of nitroaryl compounds ($RNO_2/R\dot{N}O_2^-$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
2.5.	**5-Nitroimidazoles**—Continued								
		−464	7	AQS^-	−375	*t*-BuOH	→0	C	771044
2.5.22	1-(2-*N*-Morpholinoethyl)-5-nitroimidazole (**2v**, $R^1 = CH_2CH_2$-(*N*-morpholino))	−457	7	AQS^-	−375	*t*-BuOH	→0	C	761070
2.5.23	(**2v**, $R^1 = CH_2CONH_2CH_2$-(3-pyridyl), R^4 = I)	−448	7	AQS^-	−380			C(K)	85A303
2.5.24	(**2w**, X = S)	−467	7					C	84R150
2.5.25	(**2w**, $X = SO_2$)	−342	7					C	84R150
2.6.	**Nitroazaindoles**								
2.6.1	1-Methyl-3-nitro-7-azaindole (**2x**, $R^1 = CH_3$)	−566	7	3.5.1	−700	HCO_2^-	→0		86C027
2.6.2	1-(2-Bromoethyl)-3-nitro-7-azaindole (**2x**, $R^1 = CH_2CH_2Br$))	−605	7			HCO_2^-	→0		86C027
2.6.3	(**2x**, $R^1 = CH_2CH(OH)CH_2OH$)	−607	7			HCO_2^-	→0		86C027
2.6.4	(**2x**, $R^1 = CH_2CONHCH_2CH_2OH$)	−546	7			HCO_2^-	→0		86C027
2.6.5	(**2x**, $R^1 = CH_2CONH(CH_2)_3$ -N-morpholino)	−532	7			HCO_2^-	→0		86C027
2.6.6	(**2y**, $R^7 = CH_2CO_2C_2H_5$)	−616	7			HCO_2^-	→0		86C027
2.6.7	(**2y**, $R^7 = CH_2CONH(CH_2)_3$ N morpholino)	−632	7			HCO_2^-	→0		86C027
2.6.8	(**2z**)	−626	7			HCO_2^-	→0		86C027
2.7.	**Nitroacridines**								
2.7.1	Nitroakridin 3582 (**2aa**)	−260	7	BV^{2+}	−354	2-PrOH	→0	C	84R148
2.7.2	Nitracrine (**2bb**, R^4 = H)	−275	7	BV^{2+}	−354	2-PrOH	→0	C	87R070
		−303	7	BV^{2+}	−380	2-PrOH	→0	C; further values, pH 3-11	89R018



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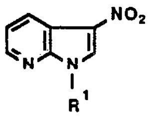

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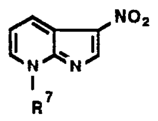

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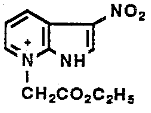

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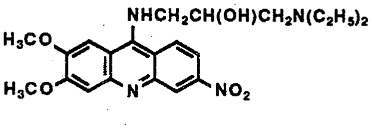

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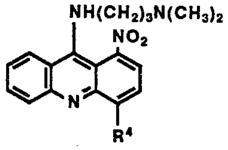

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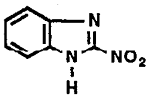
TABLE 2. Reduction potentials of nitroaryl compounds ($RNO_2/R\dot{N}O_2^-$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
2.7. Nitroacridines—Continued									
2.7.3	(**2bb**, $R^4 = Cl$)	−325	7	BV^{2+}	−380	2-PrOH	→0	C	89R018
2.7.4	(**2bb**, $R^4 = F$)	−354	7	BV^{2+}	−380	2-PrOH	→0	C	89R018
2.7.5	(**2bb**, $R^4 = CH_3$)	−321	7	BV^{2+}	−380	2-PrOH	→0	C	89R018
2.7.6	(**2bb**, $R^4 = OCH_3$)	−361	7	BV^{2+}	−380	2-PrOH	→0	C	89R018
2.7.7	(**2bb**, $R^4 = CO_2CH_3$)	−244	7	BV^{2+}	−380	2-PrOH	→0	C	89R018
2.7.8	(**2bb**, $R^4 = N(CH_3)_2$)	−334	7	BV^{2+}	−380	2-PrOH	→0	C	89R018
2.7.9	(**2bb**, $R^4 = N(CH_2CH_2OCOCH_3)_2$)	−314	7	BV^{2+}	−380	2-PrOH	→0	C	89R018
2.8. Miscellaneous nitroaryl compounds									
2.8.1	2-Nitrobenzimidazole (**2cc**)	−300	7	AQS^-	−375	2-PrOH	→0	C	80R187
2.8.2	8-Nitrotheophylline (**2dd**)	−494	7	MV^{2+}	−447		→0	C	80R187
2.8.3	8-Nitrocaffeine (**2ee**)	−205	7	DQ	−244	2-PrOH	→0	C	80R187
2.8.4	2-Nitrobenzofuran (**2ff**)	−292	7	DQ	−244	2-PrOH	~0.020	C	82R087
2.8.5	7-Hydroxy-2-nitrobenzofuran (**2ff**, $R^7 = OH$)	−288 −305	7 7	DQ AQS^-	−244 −375	2-PrOH	~0.020	C	82R087
2.8.6	7-Methoxy-2-nitrobenzofuran (**2ff**, $R^7 = OCH_3$)	−296	7	DQ	−244	2-PrOH	~0.020	C	82R087
2.8.7	5-Hydroxy-2-nitrobenzofuran (**2ff**, $R^5 = OH$)	−285 −309	7 7	DQ AQS^-	−244 −375	2-PrOH	~0.020	C	82R087
2.8.8	5-Methoxy-2-nitrobenzofuran (**2ff**, $R^5 = OCH_3$)	−292	7	DQ	−244	2-PrOH	~0.020	C	82R087
2.8.9	4-Nitropyridine (**2gg**)	−191	7	DQ	−235	2-PrOH	~0.010	C (K)	751117
2.8.10	2-Nitrothiophene (**2hh**)	−395	7	AQS^-	−380	2-PrOH	~0.010	C	751117
		−390	7	DQ	−235	2-PrOH	~0.010	C	751117
2.8.11	5-Nitrouracil (**2ii**)	−527	7	AQS^-	−380	2-PrOH	~0.010	C	751117
2.8.12	6-Hydroxy-5-nitrothymine (**2jj**)	−405	7	AQS^-	−375				80A210
2.8.13	1-Ethyl-2,3-dihydro-6-nitroimidazo[1,2-*a*]pyridinium (**2kk**, $R = C_2H_5$)	−356	7	BV^{2+}	−354	2-PrOH	→0	C	78R212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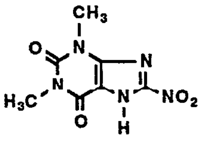
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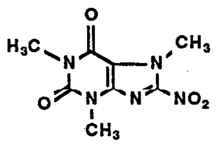
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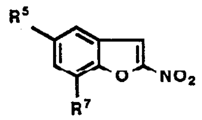
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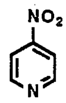
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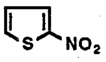
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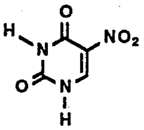
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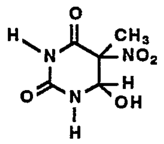
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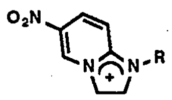
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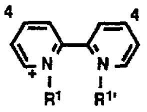
TABLE 2. Reduction potentials of nitroaryl compounds ($RNO_2/R\dot{N}O_2^-$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
2.8. Miscellaneous nitroaryl compounds—Continued									
2.8.14	1-Phenyl-2,3-dihydro-6-nitroimidazo[1,2-a]pyridinium (**2kk**, R = C_6H_5)	−335	7	BV^{2+}	−354	2-PrOH	→0	C	78R212

* Recomended value.

TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot +}$)

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.1.	**Unbridged 2,2′-bipyridinium compounds**								
3.1.1	2,2′-Bipyridinium (**3a**, $R^1 = R^{1'} = H$)	−500	(<0)	$Co(bpy)_3^{3+}$	−890	HCO_2^-		Kin.; E^o.	83C017
3.1.2	1,1′-Dimethyl-2,2′-bipyridinium (**3a**, $R^1 = R^{1'} = CH_3$)	−776	5.9-8.0					Pol., I^- salt.	67C004
		−658						Pol.	68C004, 73C001
		−720	7					Cyc. v.	80A247
3.1.3	(**3a**, $R^1 = R^{1'} = (CH_2)_3SO_3^-$)	−680						No details.	85F007
		−620	9.2					Cyc. v.	85N094
3.1.4	4,4′-Dimethyl-2,2′-bipyridinium (**3a**, $R^4 = R^{4'} = CH_3$)	−540	(<0)	$Co(bpy)_3^{3+}$	−890	HCO_2^-		Kin.; E^o.	83C017
3.2.	**Bridged 2,2′-bipyridinium compounds: derivatives of dipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium**								
3.2.1	Dipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3b**)	−270	3.4-8.6					Pol., Br^- salt.	68C002, 69C004
		−290						Pol.	68C004
3.2.2	6-Methyldipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3b**, $R^6 = CH_3$)	−300						Pol., Br^- salt.	71C001
3.2.3	6-Phenyldipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3b**, $R^6 = C_6H_5$)	−270						Pol., Br^- salt.	71C001
3.3.	**Bridged 2,2′-bipyridinium compounds: derivatives of 6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium ('diquat')**								
3.3.1	6,7-Dihydrodipyrido-[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**)	−358 *						Rec.	
		−349	10					Pot., Br^- salt.	60C001
		−354	7.8	NAD^+/NADH	−345			Enzyme-catalysed equilibrium.	65F032
		−396	2.2-11.0					Pol.	66C002
		−342						Pol.	66C001
		−360						Pol., Br^- salt.	67C003
		−349						Pol., Br^- salt.	68C004, 73C001
		−366	8.3					Pol., I^- salt.	68C001
		−366	1.6-9.2					Pol., I^- salt.	69C001
		−361						Cyc. v., Br^- and Cl^- salts.	749062
		−366						Pol., Br^- salt.	77Z190
		−370	7					Cyc. v.	80A247



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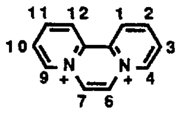

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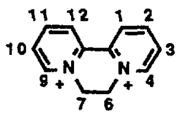


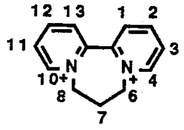
(3c)

TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot +}$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.3. Bridged 2,2′-bipyridinium compounds: derivatives of 6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium ('diquat')— Continued									
3.3.2	4-Bromo-6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^4 = Br)	−10	1.9-4.5					Pol., Br^- salt, unstable pH 7.	74C003
3.3.3	6,7-Dihydro-6-hydroxydipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^6 = OH)	−290	1.8-4.0					Pol., Br^- salt.	69C004
3.3.4	3-Cyano-6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^3 = CN)	0	2-6					Pol., Br^- salt.	76C002
3.3.5	6,7-Dihydro-4-methyldipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^4 = CH_3)	−410	4.0-9.0					Pol., Br^- salt.	77C006
3.3.6	6,7-Dihydro-6-methyldipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^6 = CH_3)	−350						Pol., Br^- salt.	71C001
3.3.7	6,7-Dihydro-3-methoxydipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^3 = OCH_3)	−450	4.5-10.4					Pol.	76C002
3.3.8	3-Methoxycarbonyl-6,7-dihydrodipyrido-[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^3 = CO_2CH_3)	−140	3-7					Pol.	76C002
3.3.9	4-Ethyl-6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^4 = C_2H_5)	−420	4.0-9.0					Pol., Br^- salt.	77C006
3.3.10	3-Ethoxy-6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^3 = OC_2H_5)	−440	4.5-10.4					Pol.	76C002
3.3.11	6,7-Dihydro-1,12-dimethyldipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^1 = R^{12} = CH_3)	−580						Pot.	60C001
		−590	7					Cyc. v.	80A247
3.3.12	6,7-Dihydro-2,11-dimethyldipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^2 = R^{11} = CH_3)	−487						Pot.	60C001
		−490	7					Cyc. v.	80A247
		−491		2.4.39	−583	2-PrOH	$\rightarrow 0$	C; Br^- salt.	84A292
3.3.13	6,7-Dihydro-3,10-dimethyldipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^3 = R^{10} = CH_3)	−479						Pot.	60C001
		−480	7					Cyc. v.	80A247
3.3.14	6,7-Dihydro-4,9-dimethyldipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^4 = R^9 = CH_3)	−480							82C019

TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot +}$)—Continued

No.	Compound or couple	*E*/mV	pH	Ref. compound	Ref. *E* /mV	Co-solute	*I*	Method/ comments	Ref.
3.3. Bridged 2,2′-bipyridinium compounds: derivatives of 6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium ('diquat')— Continued									
3.3.15	6,7-Dihydro-6,6-dimethyldipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, $R^6 = R^6 = CH_3$)	−350						Pol., Br^- salt.	71C001
3.3.16	6,7-Dihydro-3-propoxydipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, $R^3 = OC_3H_7$)	−440	4.5-10.4					Pol.	76C002
3.3.17	6,7-Dihydro-2,3,10,11-tetramethyldipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, $R^2 = R^3 = R^{10} = R^{11} = CH_3$)	−613	7	3.4.1	−548	2-PrOH	→0		84A292
3.3.18	6,7-Dihydro-4(2-pyridyl)dipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, R^4 = 2-pyridyl)	−320	1.5-8.2					Pol., Br^- salt	69C002
3.3.19	6,7-Dihydro-6-phenyldipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium (**3c**, $R^6 = C_6H_5$)	−290						Pol., Br^- salt.	71C001
3.4. Bridged 2,2′-bipyridinium compounds: derivatives of 7,8-dihydro-6*H*-dipyrido[1,2-*a*: 2′,1′-*c*][1,4]diazepinediium ('triquat')									
3.4.1	7,8-Dihydrodipyrido-[1,2-*a*:2′,1′-*c*][1,4]diazepinediium (**3d**)	−549 *						Rec.	
		−548	10					Pot., Br^- salt.	60C001
		−521	7.8					Pol.	66C001
		−550	8.3					Pol., I^- salt.	68C001
		−539	4.9-9.2						69C001
		−608						Pol.	73C001
		−556	7					Cyc. v., Br^- salt.	749062
		−550	7					Cyc. v.	80A247
		−549	7					Diff. pulse volt.; Br^- salt.	80C045
		−547	7					Pol.; Br^- salt.	80C045
		−490						Pol.; Br^- salt.	81S024
3.4.2	7,8-Dihydro-4-methyldipyrido[1,2-*a*:2′,1′-*c*]-diazepinediium (**3d**, $R^4 = CH_3$)	−590	7.0-9.0					Pol., Br^- salt.	77C006
3.4.3	7,8-Dihydro-3-methoxydipyrido[1,2-*a*:2′,1′-*c*]diazepinediium (**3d**, $R^3 = OCH_3$)	−630	4.5-10.4					Pol., Br^- salt.	76C002



(3d)

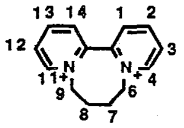
TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot+}$)—Continued

3.4. Bridged 2,2′-bipyridinium compounds: derivatives of 7,8-dihydro-6*H*-dipyrido[1,2-*a*: 2′,1′-*c*][1,4]diazepinediium ('triquat')—Continued

No.	Compound or couple	*E*/mV	pH	Ref. compound	Ref. *E* /mV	Co-solute	*I*	Method/ comments	Ref.
3.4.4	7,8-Dihydro-2,12-dimethyldipyrido[1,2-*a*:2′,1′-*c*][1,4]diazepinediium (**3d**, $R^2 = R^{12} = CH_3$)	−691 *						Rec.	
		−739						Pol., Br^- salt, meas. by T.E. Tomlinson	65C002
		−560 †	7.8					Pol., Br^- salt.	66C001
		−690						Pol.	66C001
		−690	7					Diff. pulse volt.; Br^- salt.	80C045
		−686	7					Pol.; Br^- salt.	80C045
		−630						Pol.; Br^- salt.	81S024
		−700							82C019
		−695	7	2.4.39	−583	2-PrOH	→0	C; Br^- salt.	84A292
		−686	7	3.3.17	−613	2-PrOH	→0	C; Br^- salt.	84A292
3.4.5	7,8-Dihydro-3,11-dimethyldipyrido[1,2-*a*:2′,1′-*c*]diazepinediium (**3d**, $R^3 = R^{11} = CH_3$)	−671						Pol., Br^- salt.	65C002
		−636							66C001
		−671						Pol.	66C001
		−664	7					Diff. pulse volt.; Br^- salt.	80C045
		−662	7					Pol.; Br^- salt.	80C045
3.4.6	7,8-Dihydro-2,3,11,12-tetramethyldipyrido[1,2-*a*:2′,1′-*c*][1,4]diazepinediium (**3d**, $R^2 = R^3 = R^{11} = R^{12} = CH_3$)	−770						Approx. (Value from cyc. v. in CH_3CN taken, less 30 mV.) ClO_4^- salt.	82S257
		−775	7	2.4.39	−583		→0	C; Br^- salt.	84A292
		−778	7	3.3.17	−613		→0	C; Br^- salt.	84A292

3.5. Bridged 2,2′-bipyridinium compounds: derivatives of 6,7,8,9-tetrahydrodipyrido[1,2-*a*: 2′,1′-*c*][1,4]diazocinediium ('tetraquat')

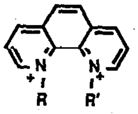
No.	Compound or couple	*E*/mV	pH	Ref. compound	Ref. *E* /mV	Co-solute	*I*	Method/ comments	Ref.
3.5.1	6,7,8,9-Tetrahydrodipyrido[1,2-*a*:2′,1′-*c*][1,4]diazocinediium (**3e**)	~-700	10					Pot., Br^- salt, cryst. with 1/2 mol HBr.	60C001
		−636	8.3					Pol., I^- salt.	68C001
		−641	6.7-9.1					Pol., I^- salt.	69C001
		−650	7					Cyc. v.	80A247



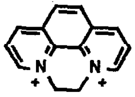
(3e)

TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot +}$)—Continued

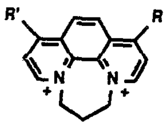
No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.5. Bridged 2,2'-bipyridinium compounds: derivatives of 6,7,8,9-tetrahydrodipyrido[1,2-a: 2',1'-c][1,4]diazocinediium ('tetraquat')—Continued									
3.5.2	6,7,8,9-Tetrahydro-2,13-dimethyl-dipyrido[1,2-*a*:2',1'-*c*][1,4]diazocinediium (**3e**, $R^2 = R^{13} = CH_3$)	−780							80A247
		−735	7	2.4.39	−583	2-PrOH	→0	C; Br^- salt.	84A292
		−745	7	3.3.17	−613	2-PrOH	→0	C; Br^- salt.	84A292
3.5.3	6,7,8,9-Tetrahydro-2,3,12,13-tetramethyl-dipyrido[1,2-*a*:2',1'-*c*][1,4]diazocinediium (**3e**, $R^2 = R^3 = R^{12} = R^{13} = CH_3$)	−832	7		−613	*t*-BuOH	→0	C; Br^- salt.	84A292
3.6. Miscellaneous 2,2'-bipyridinium compounds									
3.6.1	1,10-Phenanthrolinium (**3f**, R = R' = H)	−540						Approx., from kin. of quenching react. and comp. with bipyridyls ($E°$).	83C017
3.6.2	1,10-Dimethyl-1,10-phenanthrolinium (**3f**, $R = R' = CH_3$)	−510						Cyc. v.	*83N211*
3.6.3	Phenanthrolino[4,5-*a*:6,7-*c*]pyrazinediium (**3g**)	−280	7					Pol., Br^- salt.	68C003
		−234						Pol., Br^- salt.	68C004
		−250						Cyc. v.	83N211
3.6.4	Phenanthrolino[4,5-*a*:6,7-*c*]diazepinediium (**3h**, $R = R^1 = H$)	−270	7					Pol., Br^- salt.	68C003
		−114						Pol., Br^- salt.	68C004
		−130						Cyc. v.	83N211
		−180						Pol.; Br^- salt.	81S024
3.6.5	1-Chlorophen-anthrolino-[4,5-*a*:6,7-*c*]-diazepinediium (**3h**, R = H, R' = Cl)	−110						Pol.; Br^- salt.	81S024
3.6.6	1-Methylphen-anthrolino-[4,5-*a*:6,7-*c*]-diazepinediium (**3h**, R = H, $R' = CH_3$)	−220						Pol.; Br^- salt.	81S024
3.6.7	1,11-Dimethylphen-anthrolino-[4,5-*a*:6,7-*c*]-diazepinediium (**3h**, $R = R' = CH_3$)	−400						Pol.; Br^- salt.	81S024



(3f)



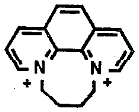
(3g)



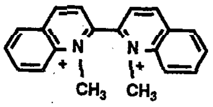
(3h)

TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot +}$)—Continued

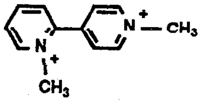
No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.6.	**Miscellaneous 2,2′-bipyridinium compounds**—Continued								
3.6.8	1,11-Diphenylphenanthrolino-{4,5-*a*:6,7-*c*}-diazepinediium (**3h**, R = R′ = C_6H_5)	−310						Pol.; Br^- salt.	81S024
3.6.9	Phenanthrolino[4,5-*a*:6,7-*c*]diazocinediium (**3i**)	−450						Cyc. v.	83N211
3.6.10	1,1′-Dimethyl-2,2′-biquinolinium (**3j**)	−250	2.2-9.9					Pol., $CH_3SO_4^-$ salt.	69C002
3.7.	**2,4′-Bipyridinium compounds**								
3.7.1	1,1′-Dimethyl-2,4′-bipyridinium (**3k**)	−640						Pot., I^- salt.	60C002
3.8.	**Symmetrical 1,1′-disubstituted 4,4′-bipyridinium compounds (viologens, $R^1 = R^{1\prime}$) without additional ring substituents**								
3.8.1	4,4′-Bipyridine (**3l**, R = H)	−485	1.5					Pol., Cl^- salt.	81Z316
3.8.2	Methyl viologen (1,1′-Dimethyl-4,4′-bipyridinium) (**3l**, R = CH_3)	−448 *						Rec.	
		−446	9-13					Pot., Cl^- salt.	33C001
		−434	1.2-13					Pol., Cl^- salt.	57C001
		−446						Pot., I^- salt.	60C002
		−426	7.8					Pol., Cl^- salt.	66C001
		−445						Pol., I^- salt.	67C002
		−418						Pol., I^- salt.	68C004, 73C001
			8.3					Pol.	68C001
		−444	9, 11					Pot.	69C003
		−454						Cyc. v.	69C005
		−443	6.8				0.11	Pol., Cl^- salt.	70C001, 81Z316
		−449						Cyc. v., Cl^- salt.	749062
		−441						Pol. or Pot., Cl^- salt.	75C001
		−464	7.45		−242			Cyc. v., At 0.1 mmol dm^{-3} viologen; value increased to −447 mV at 2 mmol dm^{-3} viologen.	76C001
		−445	11.0					Pot.	76C001
		−460	7.45					Reduct. by H_2/hydrogenase, extinction values assumed.	76C001



(3i)



(3j)



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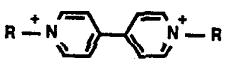


(3l)

TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot +}$)—Continued

3.8. Symmetrical 1,1′-disubstituted 4,4′-bipyridinium compounds (viologens, R^1 = $R^{1\prime}$) without additional ring substituents—Continued

No.	Compound or couple	*E*/mV	pH	Ref. compound	Ref. *E* /mV	Co-solute	*I*	Method/ comments	Ref.
		−450	7					Pol.	77Z190
		−462						Pol., bis(*O*,*O*-dimethyl phosphate) salt.	78C017
		−446						Reduct. by H_2/hydrogenase, extinction values assumed.	78C016
		−440	7					Cyc. v.	80A247
		−465	7	AQS^-	−373		→0	C; via BV^{2+}	80A349
		−456	1,7					Cyc. v.; 0.05 mol dm^{-3} H_2SO_4 or 0.5 mol dm^{-3} Na_2SO_4.	80C004
		−456						Cyc. v.	80C044
		−453						Pot.; no details.	80R192
		−430	3-12		−247			Pol.; 25 mV lower using glassy carbon electrode.	81C038
		−448	7.4					Pot.	83R178
		−436						Cyc. v.	84N047
		−479						Cyc. v.	85A301
		−450						Cyc. v.	85E687
		−458	7.0					Cyc. v.	85M420
		−446						Cyc. v.	85N197
		−441						Pot. (also data on MV^{2+} covalently linked to polymers)	86A072
3.8.3	1,1′-Dimethoxy-4,4′-bipyridinium (**31**, R = OCH_3)	−651	6.8					Pol., I^- salt.	81Z316
3.8.4	1,1′-Bis(cyanomethyl)-4,4′-bipyridinium (**31**, R = CH_2CN)	−150	6.8					Pol., I^- salt.	70C001, 81Z316
3.8.5	1,1′-Bis(carboxymethyl)-4,4′-bipyridinium (**31**, R = CH_2CO_2H)	−444						Pot.	33C001
		−410	5.0					Pol., Cl^- salt.	81Z316
3.8.6	1,1′-Bis(2-sulfonatoethyl)-4,4′-bipyridinium (**31**, R = $CH_2CH_2SO_3^-$)	−360						No details	86N260
3.8.7	1,1′-Bis(2-chloroethyl)-4,4′-bipyridinium (**31**, R = CH_2CH_2Cl)	−335	76.8					Pol. 30° C, Cl^- salt.	70C001, 81Z316
3.8.8	1,1′-Bis(carbamylmethyl)-4,4′-bipyridinium (**31**, R = CH_2CONH_2)	−296	6.8					Pol. 30° C, Cl^- salt.	70C001, 81Z316

TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot +}$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.8. Symmetrical 1,1′-disubstituted 4,4′-bipyridinium compounds (viologens, $R^1 = R^{1\prime}$) without additional ring substituents—Continued									
3.8.9	1,1′-Bis(2-hydroxyiminoethyl)-4,4′-bipyridinium (**31**, R = $CH_2CH{=}NOH$)	−325	6.8					Pol., Cl^- salt.	70C001, 81Z316
3.8.10	1,1′-Diethyl-4,4′-bipyridinium (**31**, R = C_2H_5)	−455 *						Rec.	
		−449	11.0					Pot., Cl^- salt.	33C001
		−480						Pol., See 76C001	61C001
		−466						Pol.	61M014
		−451	7					Pol.	81Z316
		−480						Pot.; no details.	80R192
3.8.11	1,1′-Bis(2-hydroxyethyl)-4,4′-bipyridinium (**31**, R = CH_2CH_2OH)	−403 *						Rec.	
		−408						Pot., Br^- salt.	60C002
		−401	1.5-9.2					Pol., Br^- salt.	69C001
		−399	6.8					Pol., Cl^- salt.	70C001, 81Z316
		−408						Cyc. v.	77C007
		−400	7					Cyc. v.	80A247
3.8.12	1,1′-Bis(2-aminoethyl)-4,4′-bipyridinium (**31**, R = $CH_2CH_2NH_2$)	−280						Pol.	81Z316
3.8.13	1,1′-Bis(2-propynyl)-4,4′-bipyridinium (**31**, R = $CH_2C{\equiv}CH$)	−435						Pol.	81Z316
3.8.14	1,1′-Bis(1,2-dichloroethyl)-4,4′-bipyridinium (**31**, R = $CH_2(Cl){=}CHCl$)	−266	6.8					Pol., Cl^- salt.	81Z316
3.8.15	1,1′-Diallyl-4,4′-bipyridinium (**31**, R = $CH_2CH{=}CH_2$)	−408						Pol.	81Z316
3.8.16	1,1′-Bis(2-oxopropyl)-4,4′-bipyridinium (**31**, R = CH_2COCH_3)	−305	1.5					Pol., Br^- salt.	81Z316
3.8.17	1,1′-Bis(2-carboxyethyl)-4,4′-bipyridinium (**31**, R = $CH_2CH_2CO_2H$)	−431						Pot., Cl^- salt.	60C002
3.8.18	1,1′-Bis(3-sulfonatopropyl)-4,4′-bipyridinium (**31**, R = $(CH_2)_3SO_3^-$)	−380 *						Rec.	
		−345						Pulse rad. and cyc. v.; 85F007 gives −370 mV (no details).	84A392
		−386						Cyc. v.	84N047
		−390	9.2					Cyc. v.	85N094

TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot +}$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.8. Symmetrical 1,1′-disubstituted 4,4′-bipyridinium compounds (viologens, R^1 = $R^{1'}$) without additional ring substituents—Continued									
3.8.19	1,1′-Dipropyl-4,4′-bipyridinium (**31**, R = n-C_3H_7)	−438						Pot., I^- salt.	60C002
		−446	3.3					Pol., Br^- salt.	75C002
3.8.20	1,1′-Bis(1-methylethyl)-4,4′-bipyridinium (**31**, R = $CH(CH_3)_2$)	−450							82C019
3.8.21	1,1′-Bis(ethylthiomethyl)-4,4′-bipyridinium (**31**, R = CH_2SEt)	−308	6.8					Pol., Cl^- salt.	81Z316
3.8.22	1,1′-Bis(3-cyanopropyl)-4,4′-bipyridinium (**31**, R = $(CH_2)_3CN$)	−362	6.8					Pol., Cl^- salt.	81Z316
3.8.23	1,1′-Bis(ethoxycarbonylmethyl)-4,4′-bipyridinium (**31**, R = CH_2CO_2Et)	−422						Pot., Cl^- salt.	60C002
		−207 *	6.8					Rec.; Pol., Br^- salt.	70C001, 81Z316
3.8.24	1,1′-Bis(dimethylaminocarbonylmethyl)-4,4′-bipyridinium (**31**, R = $CH_2CON(CH_3)_2$)	−301	1.5-9.2					Pol.	69C001
		−302	6.8					Pol., Cl^- salt.	81Z316
3.8.25	1,1′-Bis(2-ethoxyethyl)-4,4′-bipyridinium (**31**, R = CH_2CH_2OEt)	−386						Pot., I^- salt.	60C002
		−386	6.8					Pol., I^- salt.	81Z316
3.8.26	1,1′-Bis[2-(ethoxycarbonyl)ethyl]-4,4′-bipyridinium (**31**, R = $(CH_2)_2CO_2Et$)	−376	6.8					Pol., Br^- salt.	81Z316
3.8.27	1,1′-Bis[2-(dimethylaminocarbonyl)ethyl]-4,4′-bipyridinium (**31**, R = $(CH_2)_2CON(CH_3)_2$)	−385	6.8					Pol., Cl^- salt.	81Z316
3.8.28	1,1′-Bis[3-(ethoxycarbonyl)propyl]-4,4′-bipyridinium (**31**, R = $(CH_2)_3CO_2Et$)	−433	6.8					Pol., Br^- salt.	81Z316
3.8.29	1,1′-Bis[2-(trimethylammonio)ethyl]-4,4′-bipyridinium (**31**, R = $(CH_2)_2N^+(CH_3)_3$)	−280	6.8					Pol., Br^- salt.	81Z316
3.8.30	1,1′-Bis(4-nitrophenyl)-4,4′-bipyridinium (**31**, R = p-$NO_2C_6H_4$)	−150	6.8					Pol., I^- salt.	81Z316
3.8.31	1,1′-Diphenyl-4,4′-bipyridinium (**31**, R = C_6H_5)	−288	6.8					Pol., Cl^- salt.	81Z316

Table 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot +}$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.8. Symmetrical 1,1'-disubstituted 4,4'-bipyridinium compounds (viologens, $R^1 = R^{1'}$) without additional ring substituents—Continued									
3.8.32	1,1'-Bis(2-pyridylmethyl)-4,4'-bipyridinium (**31**, R = CH_2(2-pyridyl))	−325	6.8					Pol., Cl^- salt.	70C001, 81Z316
3.8.33	1,1'-Bis(diethylaminocarbonylmethyl)-4,4'-bipyridinium (**31**, R = $CH_2CON(C_2H_5)_2$)	−318							65C002
3.8.34	1,1'-Bis[3-(dimethylaminocarbonyl)propyl]-4,4'-bipyridinium (**31**, R = $(CH_2)_3CON(CH_3)_2$)	−399	6.8					Pol., Cl^- salt.	70C001, 81Z316
3.8.35	1,1'-Dihexyl-4,4'-bipyridinium (**31**, R = n-C_6H_{13})	−439						Pot., Br^- salt.	60C002
		−466	3.3					Pol., Br^- salt.	75C002
3.8.36	1,1'-Bis(2,2-diethoxyethyl)-4,4'-bipyridinium (**31**, R = $CH_2CH(OEt)_2$)	−373	6.8					Pol., Cl^- salt.	81Z316
3.8.37	1,1'-Bis[3-(trimethylammonio)propyl]-4,4'-bipyridinium (**31**, R = $(CH_2)_3N^+(CH_3)_3$)	−331	6.8					Pol., Br^- salt.	81Z316
		−330						No details	86N260
3.8.38	1,1'-Bis(α-cyanobenzyl)-4,4'-bipyridinium (**31**, R = $CH(C_6H_5)CN$)	−73	1.5, 7.0					Pol., Br^- salt.	81Z316
3.8.39	1,1'-Dibenzyl-4,4'-bipyridinium (**31**, R = $CH_2C_6H_5$)	−370 *						See introduction (Sec. 6.3)	
		−359	8.0					Pot., Cl^- salt.	33C001
		−348	1.2-13					Pol., Cl^- salt.	57C001
		−350						Pot., Cl^- salt.	60C002
		~−341	8.3					Pol.	68C001
		−335						Pol.	73C001
		−358	7.0					Cyc. v.	749062
		−329	3.3					Pol., Cl^- salt.	75C002
		−326	3.3					Pol., Br^- salt.	75C002
		−324	3.3					Pol., I^- salt.	75C002
		−330	7					Cyc. v.	80A247
		−350						Pot.; no details.	80R192
		−350	7					Pol.	81C038
		−340	6.8					Pol., Br^- salt.	81Z316
		−351	7.4					Pot.; extrap. to zero radical concn. (more positive at higher radical concn.).	83R178
3.8.40	1,1'-Diheptyl-4,4'-bipyridinium (**31**, R = n-C_7H_{15})	−356						Pol., Br^- salt.	75C002

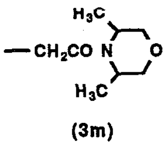
TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot +}$)—Continued

3.8. Symmetrical 1,1'-disubstituted 4,4'-bipyridinium compounds (viologens, $R^1 = R^{1'}$) without additional ring substituents—Continued

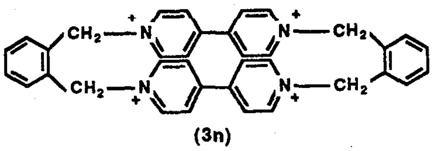
No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
		−410							82C019
3.8.41	1,1'-Bis[4-(trimethylammonio)butyl]-4,4'-bipyridinium (**3l**, R = $(CH_2)_4N^+(CH_3)_3$)	−367	8.0-10.0					Pot., Br^- salt.	81Z316
3.8.42	1,1'-Bis(α-cyanobenzyl)-4,4'-bipyridinium (**3l**, R = $CH(C_6H_5)CN$)	−73	1.5, 7.0					Pol., Br^- salt.	70C001, 81Z316
3.8.43	1,1'-Bis[2-(3,5-dimethyl-4-morpholinyl)-2-oxoethyl]-4,4'-bipyridinium (**3l**, R = **3m**)	−291	1.6-9.2					Pol., Cl^- salt.	69C001
		−305	7					Pol.	81Z316
3.8.44	1,1'-Dioctyl-4,4'-bipyridinium (**3l**, R = n-C_8H_{17})	−461	3.3					Pol., Br^- salt.	75C002
		−470						Cyc. v.	83N190
3.8.45	1,1'-Dioctadecyl-4,4'-bipyridinium (**3l**, R = n-$C_{18}H_{37}$)	−280						No details	86N260
3.8.46	1,1'-Bis[ethoxycarbonyl-(phenyl)methyl]-4,4'-bipyridinium (**3l**, R = $CH(C_6H_5)CO_2Et$)	−188	6.8					Pol., Br^- salt.	81Z316
3.8.47	(**3n**)	0	7					Cyc. v.	83N149
		−139						Cyc. v.	85A301
3.8.48	(**3o**, n = 2)	−280	7.3	3.3.1	−350	HCO_2^-	0.1	C	86A266
3.8.49	(**3o**, n = 3)	−330						Calcn.	86A266
3.8.50	(**3o**, n = 4)	−390						Calcn.	86A266

3.9. Symmetrical 1,1'-disubstituted 4,4'-bipyridinium compounds (viologens, $R^1 = R^{1'}$) with additional ring substituents

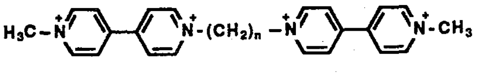
No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.9.1	1,1',2-Trimethyl-4,4'-bipyridinium (**3p**, $R^1 = R^{1'} = CH_3$, $R^2 = CH_3$)	−500	3.0-9.0					Pol., Br^- salt.	77C006



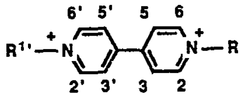
(**3m**)



(**3n**)



(**3o**)



(**3p**)

TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot +}$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.9. Symmetrical 1,1′-disubstituted 4,4′-bipyridinium compounds (viologens, $R^1 = R^{1\prime}$) with additional ring substituents—Continued									
3.9.2	1,1′-Diethyl-2-methyl-4,4′-bipyridinium (**3p**, $R^1 = R^{1\prime} = C_2H_5$, $R^2 = CH_3$)	−510	3.0-9.0					Pol., Br^- salt. 77C006	
3.9.3	2-Methyl-1,1′-dipropyl-4,4′-bipyridinium (**3p**, $R^1 = R^{1\prime} = C_3H_7$, $R^2 = CH_3$)	−500	3.0-9.0					Pol., Br^- salt.	77C006
3.9.4	2,2′-Dicyano-1,1′-dimethyl-4,4′-bipyridinium (**3p**, $R^1 = R^{1\prime} = CH_3$, $R^2 = R^{2\prime} = CN$)	90	1.9-7.0					Pol., $CH_3SO_4^-$ salt.	74C002
3.9.5	1,1′,2,2′-Tetramethyl-4,4′-bipyridinium (**3p**, $R^1 = R^{1\prime} = CH_3$, $R^2 = R^{2\prime} = CH_3$)	552	7					Pol.	70C001
		510						Approx. (Value from cyc. v. in CH_3CN taken, less 30 mV.) Cl^- salt.	82S257
3.9.6	1,1′,3,3′-Tetramethyl-4,4′-bipyridinium (**3p**, $R^1 = R^{1\prime} = CH_3$, $R^3 = R^{3\prime} = CH_3$)	−830						Approx. (Value from cyc. v. in CH_3CN taken, less 30 mV.) ClO_4^- salt.	82S257
3.9.7	1,1′,2,2′,6,6′-Hexamethyl-4,4′-bipyridinium (**3p**, $R^1 = R^{1\prime} = CH_3$, $R^2 = R^{2\prime} = CH_3$, $R^6 = R^{6\prime} = CH_3$)	−640						Approx. (Value from cyc. v. in CH_3CN taken, less 30 mV.) Cl^- salt.	82S257
3.9.8	1,1′-Dimethyl-2,2′-diphenyl-4,4′-bipyridinium (**3p**, $R^1 = R^{1\prime} = CH_3$, $R^2 = R^{2\prime} = C_6H_5$)	−390						Pol.	67C002
3.9.9	1,1′-Dimethyl-2,2′-bis(4-methylphenyl)-4,4′-bipyridinium (**3p**, $R^1 = R^{1\prime} = CH_3$, $R^2 = R^{2\prime} = C_6H_4CH_3$)	−439						Pol.	67C002
3.9.10	1,1′-Bis(cyanomethyl)-2,2′-dimethyl-4,4′-bipyridinium (**3p**, $R^1 = R^{1\prime} = CH_2CN$, $R^2 = R^{2\prime} = CH_3$)	−140	7					Pol.	70C001
3.9.11	1,1′-Bis(2-chloroethyl)-2,2′-dimethyl-4,4′-bipyridinium (**3p**, $R^1 = R^{1\prime} = CH_2CH_2Cl$, $R^2 = R^{2\prime} = CH_3$)	−422	7					Pol.	70C001
3.9.12	1,1′-Bis(2-hydroxyethyl)-2,2′-dimethyl-4,4′-bipyridinium (**3p**, $R^1 = R^{1\prime} = CH_2CH_2OH$, $R^2 = R^{2\prime} = CH_3$)	−481	7					Pol.	70C001

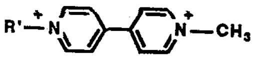
TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot +}$)—Continued

3.9. Symmetrical 1,1'-disubstituted 4,4'-bipyridinium compounds (viologens, $R^1 = R^{1'}$) with additional ring substituents—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.9.13	1,1'-Bis(2-oxopropyl)-2,2'-dimethyl-4,4'-bipyridinium (**3p**, $R^1 = R^{1'} = CH_2COCH_3$, $R^2 = R^{2'} = CH_3$)	−356	7					Pol.	70C001
3.9.14	1,1'-Bis(ethoxycarbonylmethyl)-2,2'-dimethyl-4,4'-bipyridinium (**3p**, $R^1 = R^{1'} = CH_2CO_2Et$, $R^2 = R^{2'} = CH_3$)	−323	7					Pol.	70C001
3.9.15	(**3p**, $R^1 = R^{1'} = (CH_2)_3SO_3^-$, $R^3 = R^{3'} = CH_3$)	−790	9.2					Cyc. v.	85N094
3.9.16	(**3p**, $R^1 = R^{1'} = (CH_2)_3SO_3^-$, $R^2 = R^{2'} = CH_3$)	−460	9.2					Cyc. v.	85N094
3.9.17	(**3p**, $R^1 = R^{1'} = (CH_2)_3SO_3^-$, $R^2 = R^{2'} = R^6 = R^{6'} = CH_3$)	−540	9.2					Cyc. v.	85N094

3.10. Asymmetrical 1,1'-disubstituted 4,4'-bipyridinium compounds (viologens, $R^1 = CH_3$, $R^{1'}$ = variable)

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.10.1	1-Methyl-4,4'-bipyridinium-1'-oxide (**3q**, $R' = -O^-$)	−490	6.8					Pol., $CH_3SO_4^-$ salt.	81Z316
3.10.2	1-Methyl-1'-cyanomethyl-4,4'-bipyridinium (**3q**, $R' = CH_2CN$)	−287	6.8					Pol., Cl^- salt.	70C001, 81Z316
3.10.3	1-Methyl-1'-carbamylmethyl-4,4'-bipyridinium (**3q**, $R' = CH_2CONH_2$)	−371	6.8					Pol., I^- salt.	70C001, 81Z316
3.10.4	1-Methyl-1'-(2-hydroxyethyl)-4,4'-bipyridinium (**3q**, $R' = CH_2CH_2OH$)	−422	6.8					Pol., Cl^- salt.	70C001, 81Z316
3.10.5	1-Methyl-1'-allyl-4,4'-bipyridinium (**3q**, $R' = CH_2CH{=}CH_2$)	−426	6.8					Pol., I^- salt.	81Z316
3.10.6	1-Methyl-1'-(2-oxopropyl)-4,4'-bipyridinium (**3q**, $R' = CH_2COCH_3$)	−380	6.8					Pol., I^- salt.	70C001, 81Z316
3.10.7	1-Methyl-1'-(3-cyano-2-propenyl)-4,4'-bipyridinium (**3q**, $R' = CH_2CH{=}CHCN$)	−369	6.8					Pol., I^- salt.	81Z316
3.10.8	1-Methyl-1'-[2-bis(methylthio)-ethenyl]-4,4'-bipyridinium (**3q**, $R' = CH{=}C(SCH_3)_2$)	−330	6.8					Pol., I^- salt.	81Z316



(3q)

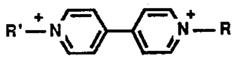
TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot+}$)—Continued

3.10. Asymmetrical 1,1'-disubstituted 4,4'-bipyridinium compounds (viologens, $R^1 = CH_3$, $R^{1'}$ = variable)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.10.9	1-Methyl-1'-ethoxycarbonylmethyl-4,4'-bipyridinium (**3q**, R' = CH_2CO_2Et)	−362	6.8					Pol., I^- salt.	70C001, 81Z316
3.10.10	1-Methyl-1'-[cyano(ethoxycarbonyl)-methyl]-4,4'-bipyridinium (**3q**, R' = $CH(CN)CO_2C_2H_5$)	−287	1.5					Pol., I^- salt.	81Z316
3.10.11	1-Methyl-1'-[3-(methoxycarbonyl)-2-propenyl]-4,4'-bipyridinium (**3q**, R' = $CH_2CH{=}CHCO_2CH_3$)	−381	6.8					Pol., I^- salt.	81Z316
3.10.12	1-Methyl-1'-[(1-pyrazolyl)thiocarbonyl-methyl]-4,4'-bipyridinium (**3q**, R' = CH_2CSNO)	−371	6.8					Pol., I^- salt.	81Z316
3.10.13	1-Methyl-1'-benzyl-4,4'-bipyridinium	−408	6.8					Pol., Br^- salt.	81Z316
3.10.14	1-Methyl-1'-[anilino(thiocarbonyl-methyl)]-4,4'-bipyridinium (**3q**, R' = $CH_2CSNHC_6H_5$)	−357	6.8					Pol., I^- salt.	81Z316
3.10.15	1-Methyl-1'-[2-(3,5-dimethyl-4-morpholinyl)-2-oxoethyl]-4,4'-bipyridinium	−374	6.8					Pol., Cl^- salt.	81Z316

3.11. Asymmetrical 1,1'-disubstituted 4,4'-bipyridinium compounds (viologens, $R^1 \neq R^{1'} \neq CH_3$)

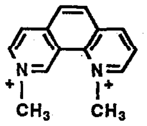
No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.11.1	1-Ethyl-1'-(2-ethylthioethyl)-4,4'-bipyridinium (**3r**, R = C_2H_5, R' = $(CH_2)_2SEt$)	−428						Pol.	81Z316
3.11.2	1-(2-Methoxycarbonylethyl)-1'-propyl-4,4'-bipyridinium (**3r**, R = C_3H_7, R' = $(CH_2)_2CO_2CH_3$)	−408						Pol.	81Z316
3.11.3	1-(2-Hydroxyethyl)-1'-pentyl-4,4'-bipyridinium (**3r**, R = C_5H_{11}, R' = CH_2CH_2OH)	−438						Pol.	81Z316
3.11.4	1-Allyl-1'-carboxymethyl-4,4'-bipyridinium (**3r**, R = $CH_2CH{=}CH_2$, R' = CH_2CO_2H)	−390						Pol.	81Z316



(3r)

TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot +}$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.11.	**Asymmetrical 1,1'-disubstituted 4,4'-bipyridinium compounds (viologens, $R^1 \neq R^{1'} \neq CH_3$)**—Continued								
3.11.5	1-Allyl-1'-ethyl-4,4'-bipyridinium (**3r**, R = $CH_2CH{=}CH_2$, R' = C_2H_5)	−428						Pol.	81Z316
3.11.6	1-Allyl-1'-(3-cyanopropyl)-4,4'-bipyridinium (**3r**, R = $CH_2CH{=}CH_2$, R' = $(CH_2)_3CN$)	−383						Pol.	81Z316
3.11.7	1-Allyl-1'-[2-(diethylaminocarbonyl)ethyl]-4,4'-bipyridinium (**3r**, R = $CH_2CH{=}CH_2$, R' = $(CH_2)_2CONEt_2$)	−383						Pol.	81Z316
3.11.8	1-(3-Butenyl)-1'-(3-cyanopropyl)-4,4'-bipyridinium (**3r**, R = $(CH_2)_2CH{=}CH_2$, R' = $(CH_2)_3CN$)	−394						Pol.	81Z316
3.11.9	1-(2-Butenyl)-1'-(3-fluoropropyl)-4,4'-bipyridinium (**3r**, R = $CH_2CH{=}CH(CH_3)$, R' = $(CH_2)_3F$)	−418						Pol.	81Z316
3.11.10	1-(Carbamylmethyl)-1'-(2-methyl-2-propenyl)-4,4'-bipyridinium (**3r**, R = $CH_2C(CH_3){=}CH_2$; R' = CH_2CONH_2)	−336						Pol.	81Z316
3.11.11	1-(2-Ethyl-2-propenyl)-1'-(2-methoxyethyl)-4,4'-bipyridinium (**3r**, R = $CH_2CH_2OCH_3$, R' = $CH_2C(Et){=}CH_2$)	−396						Pol.	81Z316
3.11.12	1-(3-Chloro-2-butenyl)-1'-(2-methoxyethyl)-4,4'-bipyridinium (**3r**, R = $CH_2CH_2OCH_3$, R' = $CH_2CH{=}C(Cl)CH_3$)	−393						Pol.	81Z316
3.12.	**Quaternary derivatives of phenanthrolines, diazapyrenes and diazapentaphenes (see also 3.6.)**								
3.12.1	1,10-Phenanthroline (see 3.6.1)	−470						Calcn.	83C017
3.12.2	1,9-Dimethyl-1,9-phenanthrolinium (**3s**)	−426						Pol.; BF_4^- salt.	73C002
3.12.3	2,8-Dimethyl-2,8-phenanthrolinium (**3t**)	−440						Pol.; BF_4^- salt.	73C002



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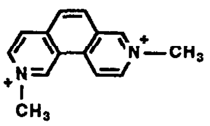
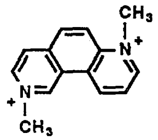


(3t)

TABLE 3. Reduction potentials of bipyridinium and related compounds ($BP^{2+}/BP^{\cdot+}$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
3.12.	**Quaternary derivatives of phenanthrolines, diazapyrenes and diazapentaphenes (see also 3.6.)**—Continued								
3.12.4	2,7-Dimethyl-2,7-phenanthrolinium (**3u**)	−302						Pol.; BF_4^- salt.	73C002
3.12.5	3,8-Dimethyl-3,8-phenanthrolinium (**3v**)	−374						Pol.; BF_4^- salt.	73C002
3.12.6	3,7-Dimethyl-3,7-phenanthrolinium (**3w**)	−406						Pol.; BF_4^- salt.	73C002
3.12.7	4,7-Dimethyl-4,7-phenanthrolinium (**3x**)	−268						Pol.; BF_4^- salt.	73C002
3.12.8	(**3y**)	−272						Pol.; BF_4^- salt.	73C002
3.12.9	(**3z**)	−300						Pol.; BF_4^- salt.	73C002
3.12.10	(**3aa**)	−228						Pol.; BF_4^- salt.	73C002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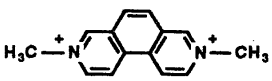
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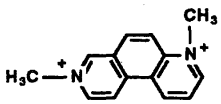
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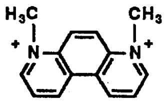
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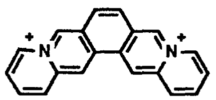
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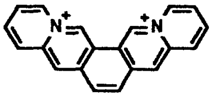
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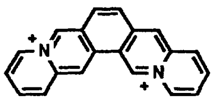
(3aa)

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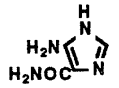
* Recomended value.

† Questionable or superseded value.

TABLE 4. Reduction potentials of miscellaneous organic compounds ($A/A^{\bullet -}$)

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
4.1.	**Aldehydes and ketones**								
4.1.1	$CH_2O/{}^{\bullet}CH_2O^-$	~−2500	≥12					Pol.	761170
		~−1600						Calcn.	80A123
		−1810		Tl^+	−1940		→0	C (+ K)	89C001
4.1.2	$CH_2O, H^+/{}^{\bullet}CH_2OH$	−920						Calcn.	75Z006
		~−970						Pol.	761170
		~−900						Calcn.	80A123
		−1180		Tl^+	−1940		→0	C (+ K)	89C001
4.1.3	$CH_3CHO/CH_3\dot{C}HO^-$	~−2500	≥12.5					Pol.	761170
		~−1800						Calcn.	80A123
		−1930		Tl^+	−1940		→0	C (+ K)	89C001
4.1.4	$CH_3CHO, H^+/ CH_3\dot{C}HOH$	~−1100						Pol.	761170
		~−1100						Calcn.	80A123
		−1250		Tl^+	−1940		→0	C (+ K)	89C001
4.1.5	$(CH_3)_2CO/(CH_3)_2\dot{C}O^-$	~−2500	≥13					Pol.	761170
		~−2100						Calcn.	80A123
		−2100		Tl^+	−1940		→0	C (+ K)	89C001
4.1.6	$(CH_3)_2CO, H^+/ (CH_3)_2\dot{C}OH$	~−1800						Pol.	761170
		~−1500						Calcn.	80A123
		−1390		Tl^+	−1940		→0	C (+ K)	89C001
4.2.	**Disulfides (RSSR)**								
4.2.1	Cystine and similar $[-SCH_2CH(NH_2)CO_2H]_2$	~−1700						Calcn.	84A044
4.2.2	β-Mercaptoethanol (oxidized) $[-SCH_2CH_2OH]_2$	−1570						Calcn.	87C020
4.2.3	Lipoamide (oxidized)	−1600						Calcn.	87C020
4.3.	**Amides**								
4.3.1	Hydroxyurea ($HONHCONH_2$)	−552 †	7	MV^{2+}	−465	2-PrOH *t*-BuOH	→0	C (high value, query).	80A349
4.3.2	4(5)-Aminoimidazole-5(4)-carboxamide (**4a**)	−584 †	7	MV^{2+}	−465	2-PrOH *t*-BuOH	→0	C (high value, query).	80A349
4.3.3	5-(3,3-Dimethyl-1-triazeno)imidazole-4-carboxamide (**4b**)	−571 †	7	MV^{2+}	−465	2-PrOH *t*-BuOH	→0	C (high value, query).	80A349
4.4.	**Pyridinium and related compounds**								
4.4.1	1-Methylnicotinamide (**4c**, $R^1 = CH_3$, $R^3 = CONH_2$, $R^4 = H$)	−936	7					Cyc. v.	74C004
		<−845	7					Pol.	76C003



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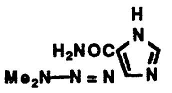

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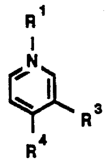
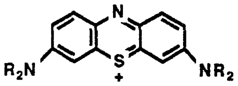


(4c)

TABLE 4. Reduction potentials of miscellaneous organic compounds (A/A•⁻)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
4.4.	**Pyridinium and related compounds**—Continued								
		−918	7	3.5.2	−735	2-PrOH	→0	C	80C008
		−1010	7	3.5.3	−832	*t*-BuOH	→0	C	84A292
4.4.2	1-Methyl-isonicotinamide (**4c**, $R^1 = CH_3$, $R^3 = H$, $R^4 = CONH_2$)	−770	7	3.5.1	−640	HCO_2^-	→0	C	80C007
4.4.3	4-Acetyl-1-methylpyridinium (**4c**, $R^1 = CH_3$, $R^3 = H$, $R^4 = COCH_3$)	−510	5					Cyc. v.	85E687
4.4.4	4-(Methoxycarbonyl)-1-methylpyridinium (**4c**, $R^1 = CH_3$, $R^3 = H$, $R^4 = CO_2CH_3$)	−720	5					Cyc. v.	85E687
4.4.5	4-Cyano-1-ethylpyridinium (**4c**, $R^1 = C_2H_5$, $R^3 = H$, $R^4 = CN$)	−626						Pol.	61M014
4.4.6	Nicotinamide adenine dinucleotide	−930	*					Rec.	
		<−730	7					Pol.	76C003
		−660 to −880	7					Pol.	76I206
		−940	7	4.4.2	−770	HCO_2^-	→0	C	80C007
		−922	7	3.5.2	−735	2-PrOH	→0	C	80C008
		−879						Calc.	82M376
		−911	9.1					Cyc. v.	84C009
4.4.7	2,2′-Bipyridine ($bpyH^+/bpyH\cdot$)	−970		$Co(bpy)_3^{2+}$	−890			K	83C017
4.4.8	4,4′-Dimethyl-2,2′-bipyridine ($Me_2bpyH^+/Me_2bpyH\cdot$)	−1050		$Co(bpy)_3^{2+}$	−890			K	83C017
4.4.9	1,10-Phenanthroline ($phenH^+/phenH\cdot$)	−850						Calcn.	83C017
4.5.	**Phenothiazinium derivatives**								
4.5.1	Thionine (**4d**, R = H)	192-200	~1.7					**Kinetics + E(Q/QH$_2$); not E^0; E(QH•/QH$_2$) = 566-575 mV at pH ~1.7.**	78A103
4.5.2	Methylene Blue (**4d**, R = CH_3)	187-197	~1.7					**Kinetics + E(Q/QH$_2$); not E^0; E(QH•/QH$_2$) = 507-516 mV at pH ~1.7.**	81A127
4.6.	**Flavins (isoalloxazines) and lumichrome derivatives (alloxazines)**								



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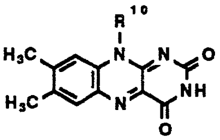
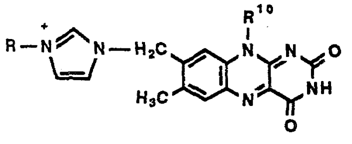


(4e)

TABLE 4. Reduction potentials of miscellaneous organic compounds ($A/A^{\bullet -}$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
4.6.	**Flavins (isoalloxazines) and lumichrome derivatives (alloxazines)**—Continued								
4.6.1	Riboflavine (**4e**, R^{10} = $CH_2[CH(OH)]_3CH_2OH$)	−292	7	DQ	−235	HCO_2^-	0.1	C + K; other values, pH 6-12.	751150
		−318	7	DQ	−247	2-PrOH	$\to 0$	C	83C002
		−317	7	AQS^-	−374	2-PrOH	$\to 0$	C	83C002
4.6.2	Flavine mononucleotide (riboflavin phosphate)	−313	7	DQ	−247	2-PrOH	$\to 0$	C; other values, pH 5-12.	83C002
		−308	7	AQS^-	−374	2-PrOH	$\to 0$		83C002
4.6.3	Flavine adenine dinucleotide (**4e**, R^{10} = 5′-adenosine diphosphate)	−241	7	BV^{2+}	−354	HCO_2^-	$\to 0$	C + K; incorrect ionic strength correction, value revised to −296 mV in 83C002.	761169
		−231	7	3.3.1	−356	HCO_2^-	$\to 0$	C + K; see above.	761169
		−308	7	DQ	−247	2-PrOH	$\to 0$	C	83C002
		−317	7	AQS^-	−374	2-PrOH	$\to 0$	C	83C002
4.6.4	8α-*N*-Imidazolylriboflavin (**4f**, R^{10} = $CH_2[CH(OH)]_3CH_2OH$, R′ = H)	−173	7.01					Pot.; other values pH 2.6-11.5	85C018
4.6.5	8α-(*N*-Methyl-*N*-imidazolium)tetra-*O*-acetylriboflavin (**4f**, R^{10} = $CH_2[CHOAc]_3CH_2OAc$, R′ = CH_3)	−118	7.29					Pot.; other values pH 2.6-10.0	85C018
4.6.6	Lumichrome (**4g**, R^1 = R^3 = H)	−502	7	AQS^- 4.4.2	−380 −770	HCO_2^- 2-PrOH	$\to 0$	C; interpolated from data at pH 2.7-4.0 (10.2-10.8).	85C005
4.6.7	1-Methyllumichrome (**4g**, R^1 = CH_3, R^3 = H)	−509	7	AQS^- 4.4.2	−380 −770	HCO_2^- 2-PrOH	$\to 0$	C; interpolated from data at pH 2.0-3.1 (8.6-10.9).	85C005
4.6.8	3-Methyllumichrome (**4g**, R^1 = H, R^3 = CH_3)	−535	7	AQS^- 4.4.2	−380 −770		$\to 0$	C; interpolated from data at pH 2.5-3.7 (9.5-10.9).	85C005
4.6.9	1,3-Dimethyllumichrome (**4g**, R^1 = R^3 = CH_3)	−530	7	AQS^- 4.4.2	−380 −770		$\to 0$	C; interpolated from data at pH 2.8-3.5 (9.8-10.5).	85C005
4.7.	**Dioxathiadiazaheteropentalenes**								
4.7.1	(**4h**, X = S)	−375						C	84A449
4.7.2	(**4h**, X = SO)	−277						C	84A449
4.7.3	(**4h**, X = SO_2)	−227						C	84A449



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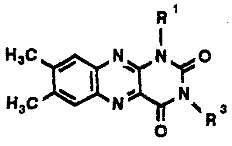

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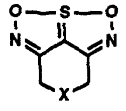
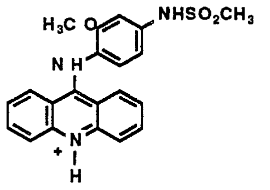


(4h)

TABLE 4. Reduction potentials of miscellaneous organic compounds (A/A•⁻)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
4.7.	**Dioxathiadiazaheteropentalenes**—Continued								
4.7.4	(**4h**, X = CH_2)	−416						C	84A449
4.8.	**Miscellaneous organic compounds**								
4.8.1	9-(2-Methoxy-4-methylsulfonylaminoanilino)-acridinium (**4i**)	−803	7	3.4.6	−775	2-PrOH	→0	C + K.	84C001
4.8.2	2,1,3-Benzothiadiazole-4,7-dicarbonitrile (**4j**)	−490	7	MV^{2+}	−447	2-PrOH			86A098
		−506	7					Cyc. v.	86A098
4.8.3	5,6-Di(2-furyl)-[1,2,5]thiadiazolo[3,4-*b*]pyrazine (**4k**, R^5 = R^6 = 2-furyl)	−374	7	BV^{2+}	−354	2-PrOH		C	87C023
4.8.4	5,6-Di(2-pyridinyl)-[1,2,5]thiadiazolo[3,4-*b*]pyrazine (**4k**, R^5 = R^6 = 2-pyridinyl)	−286	7	BV^{2+}	−354	2-PrOH		C	87C023
4.8.5	5,6-Di(2-pyridinyl)-[1,2,5]thiadiazolo[3,4-*b*]pyrazine *N*-oxide (**4k**, R^5 = 2-pyridinyl, R^6 = 2-pyridinyl-*N*-oxide)	−253	7	BV^{2+}	−354	2-PrOH		C	87C023



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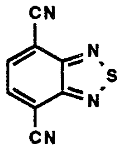

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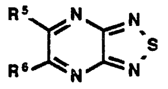

(4k)

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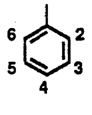
* Recomended value.

† Questionable or superseded value.

TABLE 5. Reduction potentials of phenoxyl radicals ($ArO^\bullet/ArO^-$)

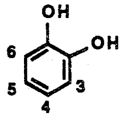
No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
5.1. Phenols									
5.1.1	Phenol (PhOH) (**5a**)	>500 †	13.5	5.3.1	300	glycol	0.5	C, ref. pot. later revised	79A100
		>600 >800	13.5 7	5.3.1	385	glycol	0.5	C calc.	82A253
		700	11.1	$SO_3^{\bullet -}$	630			C + K 900 mV calc. for pH 7.	84A327
		860	7					Cyc. v., not E°.	87C019
		800	13	ClO_2	936				88A024
	E°(PhO•, H^+/PhOH)	1352	(6.0)	7.5.1	830		$\to 0$	C	87C020
		1340						Calcn.	87C020
		1340						Calcn. from data in 84A327	87C020
5.1.2	4-Aminophenol (**5a**, $R^4 = NH_2$)	217 410	13.5 7	DMAP	174	glycol	0.5	C + K calc.	82A253
5.1.3	4-Hydroxybenzoic acid (**5a**, $R^4 = CO_2H$)	>500	13.5	5.3.1	300	glycol	0.5	C	79A100
5.1.4	*p*-Cresol (**5a**, $R^4 = CH_3$)	770	7					Cyc. v.	87C019
5.1.5	4-Methoxyphenol (**5a**, $R^4 = OCH_3$)	320 †	13.5			glycol	0.5	From 2 indicators as below	79A100
		~312 †		TMPD	82			C + K, calc. data, ref. pot. later revised to +266	79A100
		~335 †		6.1.4	183			C + K, calc. data, ref. pot. later revised to ~+330	79A100
		402 * 000	13.5 7	6.2.10	208	glycol	0.5	Rec., C + K calc.	82A253
		945	2				0.2	Cyc. v.	87C019
		655	7				0.2	Cyc. v.	87C019
		440	13				0.2	Cyc. v.	87C019
5.1.6	4-(Methylamino)phenol (**5a**, $R^4 = NHCH_3$)	146 156 146	13.5	CAT HQ TMPD	43 23 266	glycol	0.5	C + K	82A253
5.1.7	4-Acetamidophenol (**5a**, $R^4 = NHCOCH_3$)	460							88A464
5.1.8	4-(Dimethylamino)-phenol (**5a**, $R^4 = N(CH_3)_2$)	174 174	13.5	HQ CAT	23 43	glycol	0.5	C + K	82A253 (81C030)
5.1.9	Tyrosine (**5a**, $R^4 = CH_2CH(NH_2)CO_2H$)	640	13.0	6.2.9	560			Few details C + K	86A110
		1220	2					Cyc. v.	87C019
		930	7					Cyc. v.	87C019
		720	13					Cyc. v.	87C019



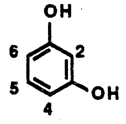
(5a)

TABLE 5. Reduction potentials of phenoxyl radicals (ArO•/ArO$^-$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
5.1.	**Phenols**—Continued								
5.1.10	DL-Tyrosine, methyl ester (**5a**, $R^4 = CH_2CH(NH_2)CO_2CH_3$)	870	7.0	6.4.4	910			Few details C + K	86A110
		660	13.0	6.2.9	560			Few details C + K	86A110
5.1.11	*N*-Acetyl-L-tyrosinamide (**5a**, $R^4 = CH_2CH(NHCOCH_3)CO_2H$)	650	12.0	6.2.9	560			Few details C + K	86A110
5.1.12	L-Alanyl-L-tyrosine (**5a**, $R^4 = CH_2CH(CO_2H)$-$NHCOCH(NH_2)CH_3$)	850	7.0	6.4.4	910			Few details C + K	86A110
5.2.	**1,2-Dihydroxybenzenes**								
5.2.1	1,2-Dihydroxybenzene (**5b**)	43	13.5	HQ	23	glycol	0.5	C + K	79A100
		139	11.0	HQ	57			Calcn.	
		98	11.0					Calcn.	
		530	7						
5.2.2	2,3-Dihydroxybenzoic acid (**5b**, $R^3 = CO_2H$)	118 *	13.5	HQ	23	glycol	0.5	Rec., C + K	79A100
		126 †		5.3.1	300			K, ref. pot. later revised	
5.2.3	3,4-Dihydroxybenzoic acid (**5b**, $R^4 = CO_2H$)	119	13.5	HQ	23	glycol	0.5	C + K	79A100
5.2.4	3,4-Dihydroxyphenylacetic acid (**5b**, $R^4 = CH_2CO_2H$)	21	13.5	DMAP	174	glycol	0.5	C	82A253 (81C030)
5.2.5	3-Hydroxytyramine (**5b**, $R^4 = CH_2CH_2NH_2$)	18	13.5	DMAP	176	glycol	0.5	C + K	82A253 (81C030)
5.2.6	Norepinephrine (**5b**, $R^4 = CH(OH)CH_2NH_2$)	44	13.5	DMAP	174	glycol	0.5	C + K	82A253 (81C030)
5.2.7	*trans*-3,4-Dihydroxycinnamic acid (**5b**, $R^4 = CH{=}CHCO_2H$)	84	13.5	DMAP	174	glycol	0.5	C + K	82A253
5.2.8	Adrenalone (**5b**, $R^4 = COCH_2NHCH_3$)	~180	13.5	DMAP	175	glycol	0.5	C	81C030
5.2.9	(**5b**, $R^4 = CH_2CH(NH_2)CO_2H$)	14 *	13.5	DMAP	174	glycol	0.5	Rec., C	81C030
		22		HQ	23			C	
5.3.	**1,3-Dihydroxybenzenes**								
5.3.1	1,3-Dihydroxybenzene (**5c**)	385 *	13.5					Rec.	
		392	13.5	DMAP	174	glycol	0.5	C + K	82A253
		379	13.5	6.2.10	208			C + K	
		810	7					Calcn.	



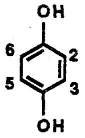
(5b)



(5c)

TABLE 5. Reduction potentials of phenoxyl radicals ($ArO\cdot/ArO^-$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
5.3.	**1,3-Dihydroxybenzenes**—Continued								
		292 †	13.5	5.2.2	118	glycol	0.5	K	79A100
		303 †		5.2.3	119			K	
		299 †			82			K, ref. potl. later revised	
5.3.2	2,5-Dihydroxybenzoic acid (**5c**, $R^4 = CO_2H$)	33	13.5	CAT	43	glycol	0.5	C + K	79A100
5.3.3	3,5-Dihydroxybenzoic acid (**5c**, $R^4 = CO_2H$)	280	13.5	5.2.3	119	glycol	0.5	C + K	79A100
5.4.	**1,4-Dihydroxybenzenes (1,4-Hydroquinones)**								
5.4.1	1,4-Dihydroxybenzene (**5d**)	1041	0					Calcn.	761063
		459	7						
		57	11					Calcn., see 751090	79A100
		23	13.5						
5.4.2	1,4-Dihydroxybenzene-2,5-disulfonate	116	12.9	HQ	23			C	85A255
5.4.3	Methylhydroquinone (**5d**, $R^2 = CH_3$)	460	7					Calcn.	761063
5.4.4	Methoxyhydroquinone (**5d**, $R^2 = OCH_3$)	−85	13.5	CAT	43	glycol	0.5	C + K	79A100
5.4.5	2',5'-Dihydroxyacetophenone (**5d**, $R^2 = COCH_3$)	118	13.5	CAT	43	glycol	0.5	C + K	79A100
5.4.6	Homogentisic acid (**5d**, $R^2 = CH_2CO_2H$)	−50	13.5	CAT	33	glycol	0.5	C + K	82A253
5.4.7	(**5d**, $R^2 = R^3 = CH_3$)	430	7					Calcn.	761063
5.4.8	(**5d**, $R^2 = R^5 = CH_3$)	980	0					Calcn.	761063
		420	7						
5.4.9	Trimethylhydroquinone (**5d**, $R^2 = R^3 = R^5 = CH_3$)	385	7					Calcn.	761063
5.4.10	Tetramethylhydroquinone (**5d**, $R^2 = R^3 = R^5 = R^6 = CH_3$)	350	7					Calcn.	74C001
		895	0					Calcn.	761063
		360	7						
		−54	13.5					Calcn., see 751090	79A100
		−54	13.5	5.2.3	119	glycol	0.5	C + K	82A253
5.5.	**Trihydroxybenzenes**								
5.5.1	1,2,3-Trihydroxybenzene (**5b**, $R^3 = OH$)	−9	13.5	HQ	23	glycol	0.5	C	79A100
5.5.2	5-Hydroxydopamine (**5b**, $R^3 = OH$, $R^5 = CH_2CH_2NH_2$)	42	13.5	DMAP	174	glycol	0.5	C + K	82A253



(5d)

TABLE 5. Reduction potentials of phenoxyl radicals (ArO·/ArO⁻)—Continued

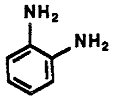
No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
5.5.	**Trihydroxybenzenes**—Continued								
5.5.3	Ethyl gallate (**5b**, $R^3 = OH$, $R^5 = CO_2C_2H_5$)	−54	13.5	HQ	23	glycol	0.5	C + K	82A253
5.5.4	1,2,4-Trihydroxybenzene (**5b**, $R^4 = OH$)	−110	13.5	CAT	43	glycol	0.5	C	79A100

* Recomended value.

† Questionable or superseded value.

TABLE 6. Reduction potentials of amine, indole, pyrimidine and purine radicals ($A^\cdot/A^-$)

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
6.1.	**Aminobenzenes and phenylenediamines**								
6.1.1	Aniline	1030	6.9	$ClO_2\cdot$	936	ClO_2^-		C	86A059
6.1.2	*N,N*-Dimethylaniline	~770	10	$SO_3\cdot^-$	630	SO_3^{2-}		C	85A103
		860	9.6	$ClO_2\cdot$	936	ClO_2^-		K	86A059
6.1.3	*o*-Phenylenediamine (**6a**)	>270	11.5	HQ	57	glycol		K	79A100
		346	13.5	TMPD	266	glycol	0.5	C + K	82A253
		362		6.1.4	309			C	
6.1.4	*p*-Phenylenediamine (**6b**)	183	13.5	HQ	23	glycol	0.5	C + K	79A100
		~200	11.0	HQ	57				
		309 *	13.5	DMAP	174	glycol	0.5	Rec., C + K	82A253
		366	13.5	TMPD	266			Au. rec.	
		340	13.5					Au. calc.	
		730	7						
		<600 *	5.2	$SO_3\cdot^-$	740	HSO_3^-		Rec., C	85A103
6.1.5	*N,N,N',N'*-Tetramethyl-*p*-phenylenediamine (**6c**)	~265	8-9					Pol. other values pH 4-8	58C002
		82 †	13.5	6.1.4	183	glycol	0.5	C + K, ref. potl. later revised	79A100
		240	7-12					Pol.	81C038
		266 *	13.5	DMAP	174	glycol	0.5	Rec., C + K	82A253
		265		6.2.10	208			C + K, E same at pH 7	
6.2.	**Indoles (IndH)**								
6.2.1	Indole (**6d**, $R^1 = R^2 = R^3 = R^5 = H$)								
	$E^\circ(IndH^{\cdot+}/IndH)$	1240		ClO_2	936	Br^-	→0	K	87A247
	$E^\circ(Ind\cdot/Ind^-)$	530						Calc. from $IndH^{\cdot+}/IndH$ and pK_a's	87A247
		970	7				0.2	Cyc. v.	87C019
6.2.2	5-Hydroxyindole (**6d**, $R^1 = R^2 = R^3 = H$, $R^5 = OH$)	216	13.5	DMAP	174	glycol	0.5	C + K	82A253
		197		TMPD	266			C + K	(81C030)
6.2.3	1-Methylindole (**6d**, $R^1 = CH_3$, $R^2 = R^3 = R^5 = H$)								
	$E^\circ(IndH^{\cdot+}/IndH)$	1230		ClO_2	936	Br^-	→0	K	88A024
6.2.4	2-Methylindole (**6d**, $R^1 = R^3 = R^5 = H$, $R^2 = CH_3$)								
	$E^\circ(IndH^{\cdot+}/IndH)$	1100		ClO_2	936	Br^-		K	88A024



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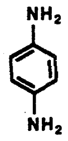

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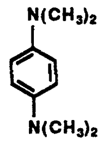

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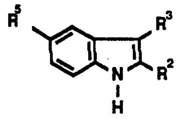
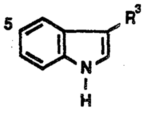


(6d)

TABLE 6. Reduction potentials of amine, indole, pyrimidine and purine radicals ($A\cdot/A^-$)—Continued

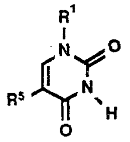
No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
6.2. Indoles (IndH)—Continued									
6.2.5	3-Methylindole (**6d**, $R^1 = R^2 = R^5 = H$, $R^3 = CH_3$)								
		1010						Calcn. (rate data + Marcus theory)	87A247
	$E^\circ(IndH^{\cdot +}/IndH)$	1070		ClO_2	936	Br^-		K	88A024
6.2.6	Indole-3-acetic acid (**6d**, $R^1 = R^2 = R^5 = H$, $R^3 = CH_2CO_2H$)	840	7					Cyc. v.	87C019
6.2.7	2,3-Dimethylindole (**6d**, $R^1 = H$, $R^2 = R^3 = CH_3$, $R^5 = H$)	780						Calcn. (rate data + Marcus theory)	87A247
	$E^\circ(IndH^{\cdot +}/IndH)$	930		ClO_2	936	Br^-		K	88A024
6.2.8	Tryptamine (**6d**, $R^1 = R^2 = R^5 = H$, $R^3 = CH_2CH_2NH_2$)								
		970	3.0	HSO_3^-	840			Few details K	86A110
		640	7.5	5.1.5	600			Few details C + K	86A110
		560	13.0	5.1.5	400			Few details C + K	86A110
6.2.9	Tryptophan (TrpH) (**6e**, $R^1 = R^2 = R^5 = H$, $R^3 = CH_2CH(NH_2)CO_2H$)								
	$E^\circ(TrpH^{\cdot +}/TrpH)$	1140		9.56	1250	SCN^-	~1	Calcn. from data in 761151, ± 200 mV	82A183
		940 †	3	HSO_3^-	840			Few details K see 86A215, 87C007	86A110
		640 †	7.5	5.1.5	600			Few details C + K see 86A215, 87C007	86A110
		560 †	13.0	5.1.5	400			Few details C + K see 86A215, 87C007	86A110
		1150	2				0.2	Cyc. v.	87C019
		1015	7				0.2	Cyc. v.	87C019
		650	13				0.2	Cyc. v.	87C019
		1080	7					Calc. from E° and pK_a	88A024
		830	7	(Fe(III))	660	N_3^-	0.15	C + K Fe(III) = ferrocinium-1,1′-dicarboxylic acid	88A126



(6e)

TABLE 6. Reduction potentials of amine, indole, pyrimidine and purine radicals ($A^{\bullet}/A^{-}$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
6.2.	**Indoles (IndH)**—Continued								
	$E^{\circ}(\mathrm{TrpH}^{\bullet+}/\mathrm{TrpH})$	1240		ClO_2	936	Br^-		K	88A024
6.2.10	5-Hydroxytryptophan (**6e**, R^3 = $CH_2CH(NH_2)CO_2H$, R^5 = OH)								
		208	13.5	DMAP	174	glycol	0.5	C + K	82A253 (81C030)
6.2.11	DL-Tryptophanamide (**6e**, R^3 = $CH_2CH(NH_2)CONH_2$)								
		940	3.0	HSO_3^-	840			Few details K	86A110
		680	7.5	5.1.5	600			Few details C + K	86A110
		620	12.0	5.1.11	650			Few details C + K	86A110
6.2.12	*N*-Acetyl-L-tryptophan (**6e**, R^3 = $CH_2CH(NHCOCH_3)CO_2H$)								
		<870	3.0	HSO_3^-	840			Few details	86A110
		690	6.5	5.1.5	600			Few details C + K	86A110
6.2.13	L-Tryptophyl-L-alanine (**6e**, R^3 = $CH_2CH(NH_2)$-$CONHCH(CH_3)CO_2H$)								
		670	7.5	5.1.5	600			Few details C + K	86A110
6.3.	**Pyrimidines**^{a}								
6.3.1	Uracil (**6f**, $R^1 = R^5 =$ H)	870	13.0	6.4.5	740	Br^-	0.2	K	86C005
		850	13.0	6.4.1	750	Br^-	0.2	K	86C005
		880	13.0	6.3.4	780	Br^-	0.2	C + K	86C005
6.3.2	1-Methyluracil (**6f**, R^1 = CH_3, R^5 = H)	~1600	13.0	9.9	1700	Br^-	0.2	C	86C005
6.3.3	Thymine (**6f**, R^1 = H, R^5 = CH_3)	780	13.0	6.4.5	740	Br^-	0.2	C + K	86C005
		800	13.0	6.4.3	630	Br^-	0.2	C + K	86C005
6.3.4	Barbituric acid (**6g**)	790	13.0	6.4.3	630	Br^-	0.2	C + K	86C005
		780	13.0	6.4.5	740	Br^-	0.2	C + K	86C005
6.3.5	Isobarbituric acid (**6h**)	132	13.5	TMPD	266	glycol	0.5	C	82A253
6.3.6	Cytosine (**6i**, R^1 = H)	830	13.0	6.4.5	740	Br^-	0.2	C + K	86C005
		790	13.0	6.4.1	750	Br^-	0.2	C + K	86C005
6.3.7	1-Methylcytosine (**6i**, R^1 = CH_3)	~1630	13.0	9.9	1700	Br^-	0.2	C	86C005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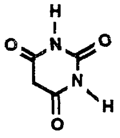
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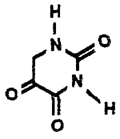
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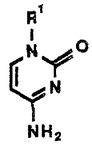
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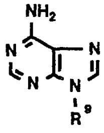
TABLE 6. Reduction potentials of amine, indole, pyrimidine and purine radicals ($A\cdot/A^-$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
6.4. Purines[a]									
6.4.1	Adenine (**6j**, $R^9 = H$)	750	13.0	6.4.3	630	Br^-	0.2	C + K	86C005
6.4.2	Adenosine (**6j**, $R^9 =$ β-D-ribofuranosyl, **6k**)	810	13.0	6.3.1	880	Br^-	0.2	C + K	86C005
6.4.3	Guanine (**6l**, $R^9 = H$)	620	13.0	6.4.6	590	Br^-	0.2	K	86C005
		650	13.0	6.2.9	570	Br^-	0.2	C + K	86C005
6.4.4	Guanosine (**6l**, $R^9 =$ β-D-ribofuranosyl, **6k**)	710	13.0	6.2.9	570	Br^-	0.2	C + K	86C005
6.4.5	Hypoxanthine (**6m**)	740	13.0	6.2.9	570	Br^-	0.2	C + K	86C005
		780	13.0	6.4.3	630	Br^-	0.2	K	86C005
6.4.6	Xanthine (**6n**)	590	13.0	5.1.5	400	Br^-	0.2	K	86C005
6.4.7	Uric acid (**6o**)	260	13.0	8.4.1	190	Br^-	0.2	C + K	86C005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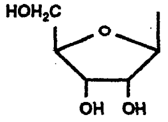
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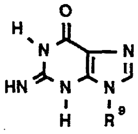
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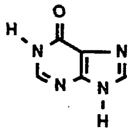
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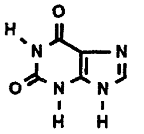
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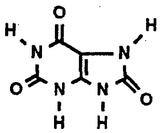
(6o)

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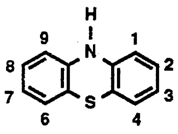
* Recomended value.

† Questionable or superseded value.

[a] Some of these data need corroboration, in view of the direct or indirect coupling to tryptophan (6.2.9) as a reference, and the comments expressed in 86A215, 87C007.

TABLE 7. Reduction potentials of phenothiazine radicals $(\mathrm{Pz}^{\cdot +}/\mathrm{Pz})$

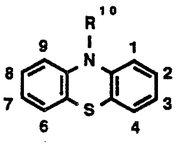
No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
7.1.	**10*H*-Phenothiazine**								
7.1.1	Phenothiazine (**7a**)	701	~2					Pot. (Br$_2$); 90% v/v AcOH.	419001
		696	~2					Pot. (Br$_2$); 80% v/v AcOH.	609013
7.2.	**10*H*-Phenothiazines with one ring carbon substituent**								
7.2.1	3-Bromophenothiazine (**7a**, R^3 = Br)	766	~2					Pot. (Br$_2$); 80% v/v AcOH.	609013
7.2.2	3-Chlorophenothiazine (**7a**, R^3 = Cl)	763	~2					Pot. (Br$_2$); 80% v/v AcOH.	609013
		776	~2					Pot. (Br$_2$); 80% v/v AcOH.	609014
7.2.3	3-Fluorophenothiazine (**7a**, R^3 = F)	722	~2					Pot. (Br$_2$); 80% v/v AcOH.	609013
7.2.4	3-Iodophenothiazine (**7a**, R^3 = I)	758	~2					Pot. (Br$_2$); 80% v/v AcOH.	609013
7.2.5	3-Nitrophenothiazine (**7a**, R^3 = NO$_2$)	~900	~2					Pot. (Br$_2$); 80% v/v AcOH.	609013
7.2.6	3-Methylphenothiazine (**7a**, R^3 = CH$_3$)	651	~2					Pot. (Br$_2$); 80% v/v AcOH.	609013
7.2.7	1-Methoxyphenothiazine (**7a**, R^1 = OCH$_3$)	698	~2					Pot. (Br$_2$); 80% v/v AcOH.	609014
7.2.8	3-Methoxyphenothiazine (**7a**, R^3 = OCH$_3$)	590	~2					Pot. (Br$_2$); 80% v/v AcOH; 2nd oxidn. at 736 mV.	609013 609014
7.2.9	1-Ethoxyphenothiazine (**7a**, R^1 = OC$_2$H$_5$)	692	~2					Pot. (Br$_2$); 80% v/v AcOH.	609014
7.2.10	3-Ethoxyphenothiazine (**7a**, R^3 = OC$_2$H$_5$)	580	~2					Pot. (Br$_2$); 80% v/v AcOH; 2nd oxidn. at 729 mV.	609014
7.2.11	3-Phenylphenothiazine (**7a**, R^3 = C$_6$H$_5$)	679	~2					Pot. (Br$_2$); 80% v/v AcOH.	609013
7.3.	**10*H*-Phenothiazines with two ring carbon substituents**								
7.3.1	2-Chloro-7-methoxyphenothiazine (**7a**, R^2 = Cl, R^7 = OCH$_3$)	662	~2					Pot. (Br$_2$); 80% v/v AcOH	609014
7.3.2	4-Chloro-7-methoxyphenothiazine (**7a**, R^4 = Cl, R^7 = OCH$_3$)	668	~2					Pot. (Br$_2$); 80% v/v AcOH	609014
7.3.3	3,7-Dimethylphenothiazine (**7a**, R^3 = R^7 = CH$_3$)	626	~2					Pot. (Br$_2$); 90% v/v AcOH	419001
		590	~2					Pot. (Br$_2$); 80% v/v AcOH	609013 609014



(7a)

TABLE 7. Reduction potentials of phenothiazine radicals ($Pz^{\cdot +}/Pz$)—Continued

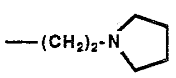
No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
7.3.	**10*H*-Phenothiazines with two ring carbon substituents**—Continued								
7.3.4	3,7-Dimethoxyphenothiazine (**7a**, $R^3 = R^7 = OCH_3$)	475	~2					Pot. (Br_2); 80% v/v AcOH.	609013
		474	~2					Pot. (Br_2); 80% v/v AcOH	609014
7.4.	***N*-Substituted phenothiazines without ring carbon substitution**								
7.4.1	10-Phenothiazinecarboxaldehyde (**7b**, $R^{10} = CHO$)	~980	~2					Pot. (Br_2); 80% v/v AcOH.	609013
7.4.2	10-Methylphenothiazine (**7b**, $R^{10} = CH_3$)	829	~2					Pot.; 80% v/v AcOH.	419001
		882	~2					Pot.; 90% v/v AcOH.	419001
		846	~2					Pot. (Br_2); 80% v/v AcOH.	609013
		~716	~1-2	Fe(III)	738		~0.02-0.2	K; stopped-flow spect. (calc. au.)	83N008
		884				CH_3CN/H_2O 80/20% v/v		Cyc. v.	86A139
7.4.3	10-Acetylphenothiazine (**7b**, $R^{10} = COCH_3$)	~960	~2					Pot. (Br_2); 80% v/v AcOH.	609013
7.4.4	(**7b**, $R^{10} = (CH_2)_3SO_3^-$)	834				CH_3CN/H_2O 80/20% v/v		Cyc. v.	86A139
7.4.5	Promazine (**7b**, $R^{10} = (CH_2)_3N(CH_3)_2$)	715						Recommended value.	
		753	~1	(NCE)				Pol.	599011
		844	<0					Pol.; 6 mol dm^{-3} H_2SO_4.	649028
		715	0	Fe(III)	738		1.0	C(+K); stopped-flow spect.	79A456
7.4.6	Promethazine (**7b**, $CH_2CH(CH_3)N(CH_3)_2$)	865						Recommended value.	
		899	~1	(NCE)				Pol.	599011
		944	<0					Pol.; 7 mol dm^{-3} H_2SO_4.	649028
		837	<0	(Ag/AgCl, KCl(s))				Chronopot.; 3 mol dm^{-3} H_2SO_4.	70M264
		865	0	Fe(III)	738		1.0	C(+K); stopped-flow spect.	79A456



(7b)

TABLE 7. Reduction potentials of phenothiazine radicals ($Pz^{\cdot +}/Pz$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
7.4. N-Substituted phenothiazines without ring carbon substitution—Continued									
7.4.7	10-(1-Methyl-2-dimethyl-aminoethyl)phenothiazine (**7b**, R^{10} = $CH(CH_3)CH_2N(CH_3)_2$)	890	0	Fe(III)	738		1.0	C(+K); stopped-flow spect.	79A456
7.4.8	10-(2-Pyrrolidinylethyl)-phenothiazine (**7b**, R^{10} = **7c**)	847	~1	(NCE)				Pol.	599011
7.4.9	(**7b**, R^{10} = $(CH_2)_6SO_3^-$)	834				CH_3CN/H_2O 80/20% v/v		Cyc. v.	86A139
7.4.10	Diethazine (**7b**, R^{10} = $(CH_2)_2N(C_2H_5)_2$)	807	<0	(Ag/AgCl, KCl(s)).				Chronopot.; 3 mol dm^{-3} H_2SO_4.	70M264
		820	0	Fe(III)	738		1.0	C(+K); stopped-flow spect.	79A456
7.4.11	Multergan (**7b**, R^{10} = $CH_2CH(CH_3)^+N(CH_3)_3$)	861	<0	(Ag/AgCl, KCl(s))				Chronopot.; 3 mol dm^{-3} H_2SO_4; $CH_3SO_4^-$ salt.	70M264
7.4.12	10-Benzoylphenothiazine (**7b**, R^{10} = COC_6H_5)	≥920						Pot. (Br_2); 80% v/v AcOH.	609013
7.4.13	10-(*N*-Methyl-3-piperidinyl)-methylphenothiazine (**7b**, R^{10} = **7d**)	783	~1	(NCE)				Pol.	599011
7.4.14	10-(2-Methyl-2-diethylaminoethyl)-phenothiazine (**7b**, R^{10} = $CH_2CH(CH_3)N(C_2H_5)_2$)	900	~1	(NCE)				Pol.	599011
7.4.15	(**7b**, R^{10} = $(CH_2)_3N(C_2H_5)_3$)	954				CH_3CN/H_2O 80/20% v/v		Cyc. v.	86A139
7.4.16	(**7b**, R^{10} = $(CH_2)_6N(C_2H_5)_3$)	864 †				CH_3CN/H_2O 80/20% v/v		Cyc. v.	86A139
7.4.17	10-[3-(4-Methyl-1-piperazinyl)-propyl]phenothiazine (**7b**, R^{10} = **7e**)	720	0	Fe(III)	738		1.0	C(+K); stopped-flow spect.	79A456
7.4.18	10-[3-(4-(2-Hydroxy-ethyl)-1-piperazinyl)propyl]-phenothiazine (**7b**, R^{10} = **7f**)	762	~1	(NCE)				Pol.	599011
7.5. N-Substituted phenothiazines with one ring carbon substituent									
7.5.1	Chlorpromazine (**7b**, R^{10} = $(CH_2)_3N(CH_3)_2$, R^2 = Cl)	780						Recommended value.	
		821	~1	(NCE)				Pol.	599011



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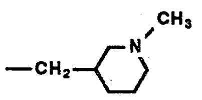

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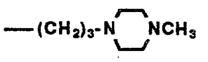

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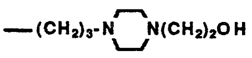

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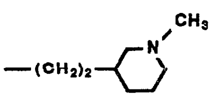
TABLE 7. Reduction potentials of phenothiazine radicals (Pz•+/Pz)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
7.5.	**N-Substituted phenothiazines with one ring carbon substituent**—Continued								
		844						Pol.; 6 mol dm^{-3} H_2SO_4.	649028
		766	<0	(Ag/AgCl, KCl(s))				Chronopot.; 3 mol dm^{-3} H_2SO_4.	70M264
		780	0	Fe(III)	738		1.0	C(+K); stopped-flow spect.	79A456
7.5.2	Triflupromazine (**7b**, $R^{10} = (CH_2)_3N(CH_3)_2$, $R^2 = CF_3$)	894	<0					Pol.; 6 mol dm^{-3} H_2SO_4.	649028
7.5.3	2-Hydroxy-10-(3-dimethylaminopropyl)phenothiazine (**7b**, $R^{10} = (CH_2)_3N(CH_3)_2$, $R^2 = OH$)	625	0	Fe(III)	738		1.0	C(+K); stopped-flow spect.	79A456
7.5.4	2-Methoxy-10-(3-dimethylaminopropyl)phenothiazine (**7b**, $R^{10} = (CH_2)_3N(CH_3)_2$, $R^2 = OCH_3$)	710	0		738		1.0	C(+K); stopped-flow spect.	79A456
7.5.5	2-Acetyl-10-(3-dimethylaminopropyl)phenothiazine (**7b**, $R^{10} = (CH_2)_3N(CH_3)_2$, $R^2 = COCH_3$)	863		(NCE)				Pol.	599011
7.5.6	Thioridazine (**7b**, R^{10} = **7g**)	794	<0					Pol.; 6 mol dm^{-3} H_2SO_4 = 30% v/v EtOH.	649028
7.5.7	Prochlorperazine (**7b**, R^{10} = **7e**)	827	~1	(NCE)				Pol.	599011
		844	<0					Pol.; 6 mol dm^{-3} H_2SO_4.	649028
7.5.8	Trifluoperazine (**7b**, R^{10} = **7e**)	944	<0					Pol.; 6 mol dm^{-3} H_2SO_4.	649028
7.5.9	Thioproperazine (**7b**, R^{10} = **7e**)	877	<0	(Ag/AgCl, KCl(s))				Chronopot.; 3 mol dm^{-3} H_2SO_4.	70M264
7.5.10	2-Chloro-10-[3-(4-(2-hydroxyethyl)-1-piperazinyl)propyl]-phenothiazine (**7b**, R^{10} = **7f**)	830	~1	(NCE)				Pol.	599011
7.6.	**Benzophenothiazines**								
7.6.1	12*H*-Benzo[*a*]phenothiazine (**7h**)	633	~2					Pot. (Br_2); 80% v/v AcOH.	609013
7.6.2	7*H*-Benzo[*c*]phenothiazine (**7i**)	628	~2					Pot. (Br_2); 80% v/v AcOH.	609013



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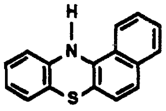

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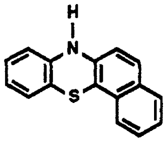
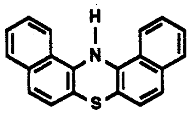


(7i)

TABLE 7. Reduction potentials of phenothiazine radicals ($Pz^{\bullet +}/Pz$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
7.6.	**Benzophenothiazines**—Continued								
7.6.3	13*H*-Dibenzo[*a,j*]phenothiazine (**7j**)	544	~2					Pot. (Br_2); 80% v/v AcOH.	609013
7.6.4	7*H*-Dibenzo[*c,h*]phenothiazine (**7k**)	548						Pot. (Br_2); 80% v/v AcOH.	609013
7.7.	**Phenothiazines with oxidized sulfur**								
7.7.1	10*H*-Phenothiazine sulfoxide (**7l**)	800	~2					Pot. (Br_2); 80% v/v AcOH.	609013
7.7.2	10*H*-Phenothiazine sulfone (**7m**, R^{10} = H)	≥900	~2					Pot. (Br_2); 80% v/v AcOH.	609013
7.7.3	10-Carbethoxyphenothiazine sulfone (**7m**, R^{10} = $CO_2C_2H_5$)	≥900	~2					Pot. (Br_2); 80% v/v AcOH.	609013



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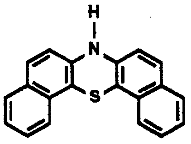

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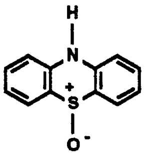

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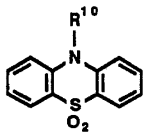

(7m)

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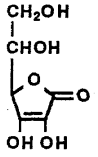
† Questionable or superseded value.

TABLE 8. Reduction potentials of radicals from miscellaneous organic compounds $(\mathrm{A}^\bullet/\mathrm{A}^-)$

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
8.1. Hydroxy compounds									
8.1.1	Ascorbic acid (**8a**)	~15	13.5	CAT	43	glycol	0.5	C	79A100
		85	11.1	CAT	139			C + K	
		300	7					Calcn.	82A253
		282	7					Calcn. not E°.	82A232
		19						Calcn.	82A232
		720						Calcn.	82A232
		330	7					Calcn. see Introduction (Sec. 5.3)	85R025
8.1.2	7-Hydroxycoumarin (**8b**)	315	13.5	DMAP	174	glycol	0.5	C + K	82A253
8.1.3	1,4-Dihydroxy-2-methylnaphthalene (**8c**)	190						Calcn.	761063
8.1.4	Vitamin K_1 (**8d**)	22	7					Calcn.	761063
8.1.5	1,2,5,8-Tetrahydroxy-9,10-anthraquinone (**8e**)	73	13.5	HQ	23	glycol	0.5	C + K	82A253
8.1.6	3,4-Dihydro-6-hydroxy-2,5,7,8-tetramethylbenzopyran-2-carboxylic acid (**8f**)	192 *	13.5	DMAP	174	glycol	0.5	Rec., C	82A253
		185	13.5	CAT	43			C + K	(81C030)
		480	7					calc.	
8.1.7	Catechin (**8g**)	79	13.5	DMAP	174	glycol	0.5	C + K	82A253
8.1.8	*l*-Epicatechin (**8h**)	48	13.5	DMAP	174	glycol	0.5	C + K	82A253
8.1.9	Quercetin (**8i**)	–37	13.5	HQ	23	glycol	0.5	C + K	82A253



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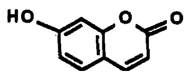
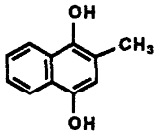
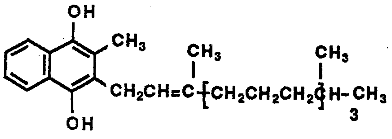


(**8b**)



(**8c**)



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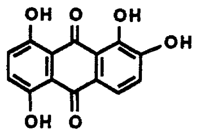

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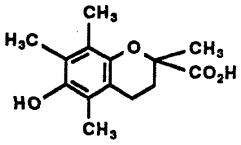

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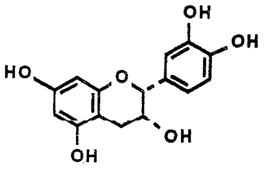

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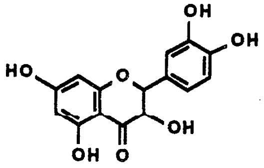

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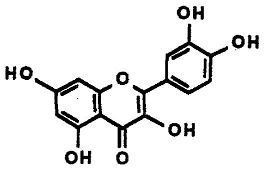

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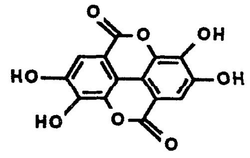


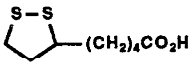
(**8j**)

TABLE 8. Reduction potentials of radicals from miscellaneous organic compounds ($A\cdot/A^-$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
8.1.	**Hydroxy compounds**—Continued								
8.1.10	Ellagic acid (**8j**)	187	13.5	HQ	23	glycol	0.5	C + K	82A253
8.2.	**Dihydronicotinamides**								
8.2.1	Nicotinamide adenine dinucleotide, reduced NAD·, H^+/NADH	282	7					Calcn. not $E°$.	80C008
		930						Kinetics + assumptions.	83M234, 84A319
8.3.	**Thiols (RSH)**								
8.3.1	**RS·/RS$^-$**								
8.3.1.1	Cysteine ($HSCH_2CH(NH_2)CO_2H$)	1100						Calcn.	84A044
		920						Calcn.	86C016
		730	9.15	GlyTyr	600			C + calc. (ref. pot. at pH 13.5, corr. for pH)	86C031
8.3.1.2	β-Mercaptoethanol ($HSCH_2CH_2OH$)	750						Calcn.	87C020
8.3.2	**RS·, H^+/RSH**								
8.3.2.1	β-Mercaptoethanol ($HSCH_2CH_2OH$)	1328	6.0	7.5.1	830		→0	C	87C020
		1342						Calcn.	87C020
8.3.2.2	Mercaptoacetic acid ($HSCH_2CO_2H$)	1347		8.3.4.4	1727		→0	C(+K)	87C020
8.3.2.3	Penicillamine ($HSC(CH_3)_2CH(NH_2)CO_2H$)	1345		8.3.4.4	1727		→0	C	87C020
8.3.2.4	3-Mercaptopropionic acid ($HSCH_2CH_2CO_2H$)	1359		8.3.4.4	1727		→0	C(+K)	87C020
8.3.3	**RSSR·$^-$/2RS$^-$**								
8.3.3.1	Cysteine	650						Calcn.	86C016
8.3.4	**RSSR·$^-$, 2H$^+$/2RSH**								
8.3.4.1	β-Mercaptoethanol	1726	9	5.1.1	1352		→0	C	87C020
		1718	10	5.1.1	1352		→0	C	87C020
8.3.4.2	Dithiothreitol ($HSCH_2[CH(OH)]_2CH_2SH$)	1752	7-10	5.1.1	1352		→0	C(+K)	87C020
		1702	7	8.3.2 (several)			→0	C(+K)	87C020
8.3.4.3	Dihydrolipoamide $HS(CH_2)_2CH(SH)(CH_2)_4$-$CONH_2$	1700	9	5.1.1	1352		→0	C	87C020
		1709	7	8.3.2.1	1335		→0	C	87C020
8.3.4.4	Dithioerythritol	1724		8.3.2.1	1359		→0	C(+K)	87C020
8.3.5	**RSSR·$^+$/RSSR**								
8.3.5.1	Dimethyl disulfide ($RSSR = CH_3SSCH_3$)	1391	~4	9.56	1331		→0	C + K	86A403

TABLE 8. Reduction potentials of radicals from miscellaneous organic compounds ($A\cdot/A^-$)—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
8.3.5	**$RSSR^{\cdot +}$/RSSR**—Continued								
8.3.5.2	Lipoic acid (RSSR = **8k**)	1130	3.6	9.29	1030			K	86A403
		1100	9	9.29	1030			K	86A403
		1140	3.6	9.56	1331			K	86A403
8.4.	**Pyrazolinones**								
8.4.1	3-Methyl-2-pyrazolin-5-one (**8l**, R^3 = CH_3, R^4 = H)	390	12.2	TMPD	270	Br^-	0.1	C + K	85A390
8.4.2	4-Methyl-2-pyrazolin-5-one (**8l**, R^3 = H, R^4 = CH_3)	320	12.2	5.1.4	400	Br^-	0.1		85A390
8.4.3	3,4-Dimethyl-2-pyrazolin-5-one (**8l**, R^3 = R^4 = CH_3)	330	12.2	5.1.4	400	Br^-	0.1	C + K	85A390
8.4.4	2,3-Dimethyl-1-phenyl-3-pyrazolin-5-one (antipyrine) (**8m**)	1200- 1500	7					K, not-equilibrium	85A390
8.5.	**Peroxy radicals**								
8.5.1	$CH_3O_2\cdot$	600-700	7-13					Prediction from rate data	86A291
8.5.2	$Cl_3CO_2\cdot$	>1000	7-13					Prediction from rate data	86A291



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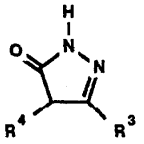

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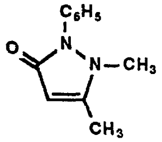

(8m)

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* Recomended value.

TABLE 9. Reduction potentials of inorganic couples

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
9.1.	aq/e_{aq}^-	−2700						Calcn.	649025
		−2900						Calcn.	730274
		−2870 *						Rec., Calcn.	81Z010
9.2.	Br·/Br$^-$	2000						Calcn.; ± 100 mV.	70C002
		2200						Calcn.	727506
		1970						Calcn.	72M258
		2080						Calcn.; ± 50 mV.	737316
		2060						Calcn.	73M369
		1760						Calcn.	761181
		~2000						Calcn.	79C029
		1904						Calcn.	82A154
		1930		9.39	1890			Calcn.; ± 30-40 mV.	84C015
		2070						Calcn.	86C016
9.3.	HBrO, H$^+$/H$_2$O, Br·	−180						Calcn.	85C012
9.4.	HBrO/Br$^-$, OH·	−360						Calcn.	85C012
9.5.	BrOH·/Br$^-$, OH$^-$	1740		9.39	1890			Calcn.; ± 30-40 mV.	84C015
9.6.	BrO$_2$·/BrO$_2^-$	1330							72M258
9.7.	BrO$_2$·, H$^+$/HBrO$_2$	1330						Calcn.	85M419
9.8.	BrO$_3^-$, 2H$^+$/BrO$_2$·, H$_2$O	1150						Calcn.	85M419
9.9.	Br$_2$·$^-$/2 Br$^-$	1660 *						Rec.	
		1900						Calcn.	727506
		1620	~1	Mn^{3+}	1550		4	Kinetics + assumptions.	737317
		1770						Calcn.; ± 50 mV.	737316
		1670						Calcn.	73M369
		1450						Calcn.	761181
		1660						Calcn.; another value: ≤1590 mV.	79C029
		1700						Calcn.	80C019
		1630		9.39	1890			Calcn.; ± 30-40 mV.	84C015
		1690						Calcn.	86C016
9.10.	Br$_2$/Br$_2$·$^-$	300						Calcn.	727506
		410						Calcn.; ± 50 mV.	737316
		510						Calcn.	73M369
		680						Calcn.	761181
		430						Calcn.	80C019
		520						Calcn.	86C016
9.11.	CN·/CN$^-$	1900						Calcn.; ± 300 mV.	70C002
		~2800						Calcn.	75Z006
9.12.	Cyanate radical ($^-$O$_2$CNHNCO$^-$)·/2NCO$^-$(?)	600-700						Prediction from rate data	87A220
9.13.	CO$_2$/CO$_2$·$^-$	~−2000						Pol.	761170
		~−2000							80A123
		−1900 *						Rec., Calcn.	85A034
		−1930						Calcn. ± ≥220 mV	87C013
		−1900		Tl$^+$	−1940		→0	C (+ K)	89C001

TABLE 9. Reduction potentials of inorganic couples—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
9.14.	$CO_2^{\cdot -}$, H^+/HCO_2^-	1070	7					Calcn. ± ≥220 mV	87C013
9.15.	$Cl^\cdot/Cl^-$	2550						Calcn.; ± 100 mV.	70C002
		2600						Calcn.	727506
		2600							
		2590						Calcn.; ± 50 mV.	737316
		2200						Calcn.	82A154
		2410		9.39	1890			Calcn.; ± 30-40 mV.	84C015
		2600						Calcn.	85C012
9.16.	HClO, H^+/H_2O, $Cl^\cdot$	−460						Calcn.	85C012
9.17.	$HClO/Cl^-$, $^\cdot OH$	−40						Calcn.	85C012
9.18.	$ClOH^\cdot/Cl^-$, OH^-	1900		9.39	1890			Calcn.; ± 30-40 mV.	84C015
9.19.	$ClO_2^\cdot/ClO_2^-$	934	4-6					Pot.	58C001
		936	4-6					Pot.	59C001
		954						Pot.	62C001
		919							65C003
		954							78Z277
		934	*					Rec., Pot.; other values 11-29°C; ± 2 mV.	85A039
9.20.	$ClO_2^\cdot$, $H^+/HClO_2$	1277	0						78Z277
		1275						Calcn.	85M419
9.21.	ClO_3^-, $2H^+/ClO_2^\cdot$, H_2O	1150						Calcn.	85M419
9.22.	$Cl_2^{\cdot -}/2\ Cl^-$	2300						Calcn.	727506
		2290						Calcn.; ± 50 mV.	737316
		2200	~1	Co^{3+}	1850		~0.2	Kinetics + assumptions; ± 60 mV.	737316
		2300						Calcn.	80C019
		2090		9.39	1890			Calcn.; ± 30-40 mV.	84C015
9.23.	$Cl_2/Cl_2^{\cdot -}$	600						Calcn.	727506
		430						Calcn.; ± 50 mV.	737316
		420						Calcn.	80C019
9.24.	$F^\cdot/F$	3600						Calcn.; ± 100 mV.	70C002
9.25.	$I^\cdot/I^-$	1270						Calcn.; no details.	63F022
		1400						Calcn.; ± 50 mV.	70C002
		1400						Calcn.	727506
		1310						Calcn.; ± 50 mV.	737316
		1420						Calcn.	73M369
		1380	~1.3	$Os(bpy)_3^{3+}$	840		1	Kinetics.	78A485
		1330						Kinetics + assumptions.	80A447
		1280	~3.5	7.4.6	865		~0.1	C + K	83A273
		1410						Calcn.	86C016
		1330		9.41	−330			$HO_2^\cdot/I_2$ reaction; C + K + calcn.	86A070

TABLE 9. Reduction potentials of inorganic couples—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
9.26.	$ICl_2^{\cdot -}/I_2$, 2 Cl^-	1056							78Z277
9.27.	HIO, H^+/H_2O, I·	−160						Calcn.	85C012
9.28.	HIO/I^-, ·OH	−1040						Calcn.	85C012
9.29.	$I_2^{\cdot -}/2\ I^-$	1040						Calcn.; no details.	63F022
		1100						Calcn.	727506
		1000						Calcn.; ± 50 mV.	737316
		1130						Calcn.	73M369
		1080	~1.3	$Os(bpy)_3^{3+}$	840		1	Kinetics + calcn.	78A485
		1000						Calcn.	80C019
		1040		9.25	1330			Calcn.	80A447
		1063	~3	$Os(bpy)_3^{3+}$	857		0.1	Kinetics; ± 11 mV.	82A115
		981	~3.5	7.4.6	865		~0.1	C + K	83A273
		1130						Calcn.	86C016
		1030		9.41	−330			$HO_2^{\cdot}/I_2$ reaction; C + K + calcn.	86A070
9.30.	$I_2/I_2^{\cdot -}$	300						Calcn.	727506
		60						Calcn.; ± 50 mV.	737316
		110						Calcn.	73M369
		160						Calcn.	78A485
		200						Calcn.	83C019
		110						Calcn.	86C016
		210		9.41	−330			$HO_2^{\cdot}/I_2$ reaction; C + K	86A070
9.31.	$IO_2^{\cdot}$, H^+/HIO_2	1000						Calcn.	76M471
9.32.	IO_3^-, $2H^+/IO_2^{\cdot}$, H_2O	800						Calcn.	76M471
9.33.	$N_3^{\cdot}/N_3^-$	1330 *						Rec.	
		~1900						Calcn.	75Z006
		1370						Calcn.; ± 220 mV.	83C030
		1330	6.5	$IrCl_6^{2-}$	930		1.0	K	85C023 (86A223)
		1350		9.9	1630	Br^-	2-3		87C002
		1320						Cyc. v.; ± 30 mV	87C002
		≤1365		9.10	510			Calcn.	87M124
9.34.	$N_6^{\cdot -}/2N_3^-$	1930		9.33	1900			C	84A013
9.35.	$N_2H_4^{\cdot +}/N_2H_4$	≤730		$Fe(CN)_6^{3-}$				Kinetics + assumptions.	84A237
9.36.	$\cdot NO_2/NO_2^-$	1000 870						Calcn.; ± 100 mV.	70C002
		910						Calcn.	82C006
		1030						Calcn.; ± 40 mV.	83C030
		1040		$Fe(TMP)_3^{2+}$			0.3	TMP = 3,4,7,8-tetramethyl-phenanthroline	85A480
		870						Calcn.	85C012
9.37.	$NO_3^{\cdot}/NO_3^-$	2300						Calcn.; ± 100 mV.	70C002
		~1900						Calcn.	75Z006
		2300-2600						Prediction based on rate data	86A278
9.38.	·OH, H^+/H_2O	2730 *						Rec.	

TABLE 9. Reduction potentials of inorganic couples—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
		1800	7					Calcn.; not E°.	769245
		2850	0					Calcn.	78Z277
		2180	7					Calcn.; not E°.	82C006
		2590	0					Calcn.	84C002
		2720	0	Tl^{2+}	2220			$Tl^+/{\cdot}OH$ reaction (kinetics); ± 20 mV.	84C015
		2740	0	9.19	934			ClO_2^-/O_3 reaction (kinetics), + calcn.	85A039
9.39.	${\cdot}OH/OH^-$	1900 *						Rec.	
		1900						Calcn.; ± 100 mV.	70C002
		2020							78Z277
		1770						Calcn.	84C002
		1890		Tl^{2+}	2220			$Tl^+/{\cdot}OH$ reaction (kinetics) ± 20 mV.	84C015
		1910		9.19	934			ClO_2^-/O_3 reaction (kinetics), + calcn.; ± 10 mV.	85A039
9.40.	$O{\cdot}^-$, $H_2O/2\ OH^-$	1870						Calcn.	80C019
		1760		Tl^{2+}	2220			$Tl^+/{\cdot}OH$ reaction (kinetics), + calcn.; ± 20 mV.	84C015
		1780		9.19	934			ClO_2^-/O_3 reaction (kinetics), + calcn.	85A039
9.41.	$O_2/O_2{\cdot}^-$	−330 *						Rec.	
		−330						Calcn.	72C001
		−288						Pol.; −532 mV vs SCE	72C002
		−330		DQ	−250			Calcn.	74C001
		−330	7.2	1.1.4	−67	HCO_2^-	0.1	C(+K).	741141
		−310		DQ				Calc. from data in 730125.	741141
		−325	7	DQ	−235	HCO_2^-		C; −155 mV for 1 mol dm^{-3} O_2.	751090
		−330	7	1.1.1	100			Kin. reaction QH_2 + H_2O_2 cat. peroxidase.	75C004
9.42.	O_2, $H^+/HO_2{\cdot}$	−37 −50	0					Calcn.	761063
		−50						Calcn.	85C012
9.43.	$O_2(^1\Delta_g)/O_2{\cdot}^-$	650	7						769245
9.44.	$O_2{\cdot}^-$, H^+/HO_2^-	1000						Calcn.	761063
9.45.	$O_2{\cdot}^-$, $2\ H^+/H_2O_2$	1710 1760	0					Calcn.	761063
		1760						Calcn.	85C012
9.46.	$O_2{\cdot}^-$, $2\ H^+/H_2O_2$	940	7					Calcn.; ± 20 mV, not E°.	74C001
		865	7					Calcn.; not E°.	751090
		940	7					Calcn.; not E°.	769245

TABLE 9. Reduction potentials of inorganic couples—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
9.47.	$HO_2\cdot$, H^+/H_2O_2	1420 1480	0					Calcn.; not E°.	761063
		1495	0					Calcn.	78Z277
		1480						Calcn.	85C012
9.48.	$HO_2\cdot/HO_2^-$	790						Calcn.	85C012
9.49.	H_2O_2, $H^+/H_2O,\cdot OH$	800 870	7					Calcn.; not E°.	769245
		460	7					Calcn.; not E°.	82C006
		460-520	7					Calcn.; not E°.	84C002
		870						Calcn.	85C012
9.50.	$O_3/O_3\cdot^-$	1600 1040	≥11					Calcn.; ± 100 mV.	82C006
		1190	≥11					Calcn.	84C002
		1010 *	11-12	9.19	934			Rec., ClO_2^-/O_3 reaction (kinetics).	85A039
		1040						Calcn.	85C012
9.51.	O_3, $H^+/HO_3\cdot$	1800	7					Calcn.; not E°.	82C006
9.52.	S, $H^+/HS\cdot$	~−1300	0					Calcn.	87A082
9.53.	$HS\cdot/HS^-$	1150						Calcn.	86C016
9.54.	$HSSH\cdot/2HS^-$	900						Calcn.	86C016
9.55.	$SCN\cdot/SCN^-$	1620	~1.3	$Fe(bpy)_3^{3+}$	1065		1	Kinetics (one rate const. assumed).	78A485
		1680	~1.3	$Os(bpy)_3^{3+}$	837		1	Kinetics + calcn. (some assumptions).	78A485
		1650		9.25	1380			Calcn.	78A485
		1660		9.25	1330			Calcn.	80A447
		1601						Calcn.	82A154
		1620						Calcn.	86A070
		1660		6.2.9	1240			Calcn.	88A024
9.56.	$(SCN)_2\cdot^-/2\ SCN^-$	1330 *						Rec.	
		1310	~1.3	$Fe(bpy)_3^{3+}$	1065		1	Kinetics + calcn. (rate const. assumed).	78A485
		1370	~1.3	$Os(bpy)_3^{3+}$	837		1	Kinetics + calcn. (some assumptions).	78A485
		1290		9.55	1660			Calcn.	80A447
		1250		9.29	1000			Calcn.; ± 220 mV.	82A183
		1331	~3	$Os(bpy)_3^{3+}$	857		0.1	Kinetics; ± 8 mV.	82A115
		1310						Calcn.	86A070
		1350		6.2.9	1240			Calcn.	88A024
9.57.	$(SCN)_2/(SCN)_2\cdot^-$	540						Calcn.	78A485
9.58.	$SO_2/SO_2\cdot^-$	−262 −280						Calcn.	84A454
		−280						Calcn.	85C012
		−288	1					Cyc. v.	87A083
9.59.	$SO_2\cdot^-$, H_2O/HSO_3^-, H^+	−660	7					$S_2O_4^{2-}/MV^{2+}$ reaction + calcn.; not E°.	78C016

TABLE 9. Reduction potentials of inorganic couples—Continued

No.	Compound or couple	E/mV	pH	Ref. compound	Ref. E /mV	Co-solute	I	Method/ comments	Ref.
9.60.	$\dot{S}O_3^-/SO_3^{2-}$	630	≥8					Calc. from value at pH 3.6	84A327
		760	11	9.19	936		→0		88A024
9.61.	$\dot{S}O_3^-/HSO_3^-$	840	3.6	7.5.1	780		~0.1	C	84A327
9.62.	SO_4^{2-}, $H_2O/\dot{S}O_3^-$, $2OH^-$	−2470						Calcn.	84A327
9.63.	$SO_4^{\cdot -}/SO_4^{2-}$	~2430						Calcn. (see ref.)	89Z064
9.64.	$SO_5^{\cdot -}/HSO_5^-$	~1100	6.7	9.29	1130			Equilibrium not attained.	84A327
9.65.	$S_2O_3^{\cdot -}/S_2O_3^{2-}$	1340						Calcn.	82A154
		1350 1600						Calcn.	83C030
		1600						Calcn.	85C012
9.66.	SeO_3^-/SeO_3^{2-}	1680						K + calcn.	86A335
9.67.	SeO_3^-, $H^+/HSeO_3^-$	2180						K + calcn.; further calcns. of related couples	86A335
9.68.	$(SeCN)_2^{\cdot -}/2\ SeCN^-$	900-1000						Calcn. + assumptions.	79A035

* Recomended value.

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14. Compound Name Index

15. Molecular Formula Index