Reduction Potentials of Radicals

David M. Stanbury, task group leader, Auburn University, USA

Objective:

To evaluate standard potentials ($E°$) and related quantities for important aqueous organic and inorganic radicals.

Current status:

Recommendations have been made for

40 inorganic $E°$s

38 organic $E°$'s

22 inorganic $\Delta_f G°$'s

17 inorganic pK_a' s

11 inorganic hemicolligations

60 inorganic equilibria

☐A web site has been created.

Sample summary pages from web site:

Table 1: Inorganic reduction potentials

	Half-reaction	Electrode Potential, V	Comments	Full details
	Table 1.1: Electron, Hydrogen and Oxygen			
1.1.01	$e^- = e^{\bullet-}(aq)$	-2.89 ± 0.03		initial
1.1.02	$H^+ + e^- = H^{\bullet}(aq)$	-2.32 ± 0.03		initial
1.1.1	$O(^3P) + e^- = O^{\bullet-}$	$+(1.6 \pm 0.1)$		initial
1.1.1a	$O(^3P) + H^+ + e^- = HO^{\bullet}$	$+(2.3 \pm 0.1)$		initial
1.1.2	$O_2(g) + e^- = O_2^{\bullet-}$	$-(0.35 \pm 0.01)$		initial
1.1.3	$O_2(aq) + e^- = O_2^{\bullet-}$	$-(0.18 \pm 0.01)$	$K_H = 1.27 \times 10^{-3}$	initial
1.1.4	$^1\Delta_g O_2(g) + e^- = O_2^{\bullet-}$	$+(0.64 \pm 0.01)$		initial
1.1.5	$^1\Delta_g O_2(aq) + e^- = O_2^{\bullet-}$	$+(0.81 \pm 0.01)$	$K_H = 1.27 \times 10^{-3}$ (assumed)	initial
1.1.6	$O_2(g) + e^- + H^+ = HO_2^{\bullet}$	$-(0.07 \pm 0.01)$		initial
1.1.7	$O_2(aq) + H^+ + e^- = HO_2^{\bullet}$	$+(0.10 \pm 0.01)$	$K_H = 1.27 \times 10^{-3}$, p$K_a$ = 4.8	initial

Table 6: Hemicolligation Equilibria

Reaction	K, M^{-1}	Link and status
$O_2(aq) + O^{\bullet-} = O_3^{\bullet-}$	$(1.4 \pm 0.1) \times 10^6$	initial
$Cl^{\bullet}(aq) + Cl^- = Cl_2^{\bullet-}$	$(1.4 \pm 0.2) \times 10^5$	final
$OH^{\bullet}(aq) + Cl^- = ClOH^{\bullet-}$	0.70 ± 0.13	final
$Br^{\bullet}(aq) + Br^- = Br_2^{\bullet-}$	$(3.9 \pm 30\%) \times 10^5$	final
$OH^{\bullet}(aq) + Br^- = BrOH^{\bullet-}$	$(3.2) \times 10^2$ within factor of 2	final
$HAsO_3^{\bullet-} + H_2O = As(OH)_3O^{\bullet-}$	p$K = 3.53 \pm 0.11$	initial
$Tl^+ + OH^{\bullet}(aq) = TlOH^{\bullet+}$	$(5.8 \pm 1.0) \times 10^3$	initial
$Tl^{\bullet 2+} + Cl^- = TlCl^{\bullet+}$	$(6.2 \pm 0.7) \times 10^4$	initial
$TlCl^{\bullet+} + Cl^- = TlCl_2^{\bullet}$	$(1.9 \pm 0.4) \times 10^3$	initial
$TlCl_2^{\bullet} + Cl^- = TlCl_3^{\bullet-}$	13 ± 3	initial

Sample evaluation

Reaction number = 3.46
Chemical equilibrium = $OH + Cl^- + H^+ \rightleftharpoons Cl + H_2O$

List of reports:

$K_{eq} = (2.0 \pm 1.0) \times 10^5\ M^{-2}$, $\mu = 0.01$ M. [1] Result obtained from UV/vis data on the equilibrium attained during pulse-radiolysis. The value they report takes the concentration of water into account; the value given here has been corrected to reflect water having unit activity.

$K_{eq} = 9.1 \times 10^4\ M^{-2}$, no specified uncertainty but probably good within a factor of 2, $\mu = 0.01$ M.[2] The basis for this result is unclear from the published paper, but a letter from Kläning to Stanbury (Feb, 21, 1990) clarifies things: it states that the result was obtained by recalulation from the optical/pulse-radiolysis data of Jayson et al.[1] with a correction for the optical density due to chlorine atoms.

Discussion

McElroy has argued that the decay of chlorine atoms is more complex than indicated by the models of Jayson et al. and Kläning et al., and he has specifically introduced the equilibrium hydration of chlorine atoms: $Cl(aq) + H_2O(l) \rightleftharpoons HOClH$.[3] However, Buxton et al. have argued pursuasively that McElroy's suggestion is unsupported by the data.[4]

We accept the result of Kläning et al., with the understanding that it hasn't been checked directly and that it is likely to be dependent on ionic strength.

Recommended value: $K_{eq} = 9.1 \times 10^4\ M^{-2}$ within a factor of two at $\mu = 0.01$ M.

List of auxiliary thermo data: none

Revision of 5/14/03, DMS. checked by ???

References

(1) Jayson, G.; Parsons, B. J.; Swallow, A. J. *J. Chem. Soc., Faraday Trans. I* **1973**, *69*, 1597-1607.
(2) Kläning, U. K.; Wolff, T. *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 243-245.
(3) McElroy, W. J. *J. Phys. Chem.* **1990**, *94*, 2435-2441.