REDUCTION AND OXIDATION POTENTIALS FOR CERTAIN ION RADICALS

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There are two tables for ion radicals. The first table lists reduction potentials for organic compounds which produce anion radicals during reduction, a process described as $A + e^- \rightleftharpoons A^{-\cdot}$. The second table lists oxidation potentials for organic compounds which produce cation radicals during oxidation, a process described as $A \rightleftharpoons A^{+\cdot} + e^-$. To obtain reduction potential for a reverse reaction, the sign for the potential is changed.

Unlike the table of the Electrochemical Series, which lists *standard* potentials, values for radicals are experimental values with experimental conditions given in the second column. Since the measurements leading to potentials for ion radicals are very dependent on conditions, an attempt to report standard potentials for radicals would serve no useful purpose. For the same reason, the potentials are also reported as experimental values, usually a half-wave potential ($E_{1/2}$ in polarography) or a peak potential (E_p in cyclic voltammetry). Unless otherwise stated, the values are reported vs. SCE (saturated calomel electrode). To obtain a value vs. normal hydrogen electrode, 0.241 V has to be added to the SCE values. All the ion radicals chosen for inclusion in the tables result from electrochemically reversible reactions. More detailed data on ion radicals can be found in the *Encyclopedia of Electrochemistry of Elements*, (A. J. Bard, Ed.), Vol. XI and XII in particular, Marcel Dekker, New York, 1978.

Abbreviations are: CV — cyclic voltammetry; DMF — *N*,*N*-Dimethylformamide; *E* swp — potential sweep; E° — standard potential; E_p — peak potential; $E_{p/2}$ — half-peak potential; $E_{1/2}$ — half wave potential; *M* — mol/L; MeCN — acetonitrile; pol — polarography; rot Pt dsk — rotated Pt disk; SCE — saturated calomel electrode; $TBABF_4$ — tetrabutylammonium tetrafluoroborate; TBAI — tetrabutylammonium iodide; TBAP — tetrabutylammonium perchlorate; TEABr — tetraethylammonium bromide; TEAP — tetraethylammonium perchlorate; THF — tetrahydrofuran; $TPACF_3SO_3$ — tetrapropylammonium trifluoromethanesulfite; TPAP — tetrapropylammonium perchlorate; and wr — wire.

Reduction Potentials (Products are Anion Radicals)

Substance	Conditions/electrode/technique	Potential V (vs. SCE)
Acetone	DMF, 0.1 *M* TEABr/Hg/pol	$E_{1/2} = -2.84$
1-Naphthyphenylacetylene	DMF, 0.03 *M* TBAI/Hg/pol	$E_{1/2} = -1.91$
1-Naphthalenecarboxyaldehyde	-/Hg/pol	$E_{1/2} = -0.91$
2-Naphthalenecarboxyaldehyde	-/Hg/pol	$E_{1/2} = -0.96$
2-Phenanthrenecarboxaldehyde	-/Hg/pol	$E_{1/2} = -1.00$
3-Phenanthrenecarboxaldehyde	-/Hg/pol	$E_{1/2} = -0.94$
9-Phenanthrenecarboxaldehyde	-/Hg/pol	$E_{1/2} = -0.83$
1-Anthracenecarboxaldehyde	-/Hg/pol	$E_{1/2} = -0.75$
1-Pyrenecarboxaldehyde	-/Hg/pol	$E_{1/2} = -0.76$
2-Pyrenecarboxaldehyde	-/Hg/pol	$E_{1/2} = -1.00$
Anthracene	DMF, 0.1 *M* TBAP/Pt dsk/CV	$E_p = -2.00$
	DMF, 0.5 *M* $TBABF_4$/Hg/CV	$E_{1/2} = -1.93$
	MeCN, 0.1 *M* TEAP/Hg/CV	$E_{1/2} = -2.07$
	DMF, 0.1 *M* TBAI/Hg/pol	$E_{1/2} = -1.92$
9,10-Dimethylanthracene	DMF, 0.1 *M* TBAP/Pt/CV	$E_p = -2.08$
	MeCN, 0.1 *M* TBAP/Pt/CV	$E_p = -2.10$
1-Phenylanthracene	DMF, 0.5 *M* $TBABF_2$/Hg/CV	$E_{1/2} = -1.91$
	DMF, 0.1 *M* TBAI/Hg/pol	$E_{1/2} = -1.878$
2-Phenylanthracene	DMF, 0.1 *M* TBAI/Hg/pol	$E_{1/2} = -1.875$
8-Phenylanthracene	DMF, 0.5 *M* $TBABF_4$/Hg/CV	$E_{1/2} = -1.91$
9-Phenylanthracene	DMF, 0.5 *M* $TBABF_4$/Hg/CV	$E_{1/2} = -1.93$
	DMF, 0.1 *M* TBAI/Hg/pol	$E_{1/2} = -1.863$
1,8-Diphenylanthracene	DMF, 0.5 *M* $TBABF_4$/Hg/CV	$E_{1/2} = -1.88$
1,9-Diphenylanthracene	DMF, 0.1 *M* TBAI/Hg/pol	$E_{1/2} = -1.846$
1,10-Diphenylanthracene	DMF, 0.1 *M* TBAI/Hg/pol	$E_{1/2} = -1.786$
8,9-Diphenylanthracene	DMF, 0.5 *M* $TBABF_4$/Hg/CV	$E_{1/2} = -1.90$
9,10-Diphenylanthracene	MeCN, 0.1 *M* TBAP/rot Pt/E swp	$E_{1/2} = -1.83$
	DMF, 0.1 *M* TBAI/Hg/pol	$E_{1/2} = -1.835$
1,8,9-Triphenylanthracene	DMF, 0.5 *M* $TBABF_4$/Hg/CV	$E_{1/2} = -1.85$
1,8,10-Triphenylanthracene	DMF, 0.5 *M* $TBABF_4$/Hg/CV	$E_{1/2} = -1.81$
9,10-Dibiphenylanthracene	MeCN, 0.1 *M* TBAP/rot Pt/E swp	$E_{1/2} = -1.94$
Benz(a)anthracene	MeCN, 0.1 *M* TEAP/Hg/CV	$E_{1/2} = -2.11$
	MeCN, 0.1 *M* TEAP/Hg/pol	$E_{1/2} = -2.40^a$
Azulene	DMF, 0.1 *M* TBAI/Hg/pol	$E_{1/2} = -1.10^c$
Annulene	DMF, 0.5 *M* TBAP 0°C/Hg/pol	$E_{1/2} = -1.23$
Benzaldehyde	DMF, 0.1 *M* TBAP/Hg/pol	$E_{1/2} = -1.67$
Benzil	DMSO, 0.1 *M* TBAP/Hg/pol	$E_{1/2} = -1.04$

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REDUCTION AND OXIDATION POTENTIALS FOR CERTAIN ION RADICALS (continued)

Reduction Potentials (Products are Anion Radicals) (continued)

Substance	Conditions/electrode/technique	Potential V (vs. SCE)
Benzophenone	-/Hg/pol	$E_{1/2}$ = –1.80
	DMF/Pt dsk/CV	E° = –1.72
Chrysene	MeCN, 0.1 *M* TEAP/Hg/pol	$E_{1/2}$ = –2.73[a]
Fluoranthrene	DMF, 0.1 *M* TBAP/Pt dsk/CV	E_p = –1.76
Cyclohexanone	DMF, 0.1 *M* TEABr/Hg/pol	$E_{1/2}$ = –2.79
5,5-Dimethyl-3-phenyl-2-cyclohexen-1-one	DMF, 0.5 *M*/Hg/pol	$E_{1/2}$ = –1.71
1,2,3-Indanetrione hydrate (ninhydrin)	DMF, 0.2 *M* $NaNO_3$/Hg/pol	$E_{1/2}$ = –0.039
Naphthacene	DMF, 0.1 *M* TBAI/Hg/pol	$E_{1/2}$ = –1.53
Naphthalene	DMF, 0.1 *M* TBAP/Pt dsk/CV	E_p = –2.55
	DMF, 0.5 *M* $TBABF_4$/Hg/CV	$E_{1/2}$ = –2.56
	DMF, MeCN, 0.1 *M* TEAP/Hg/CV	$E_{1/2}$ = –2.63
	DMF, 0.1 *M* TBAI/Hg/pol	$E_{1/2}$ = –2.50
1-Phenylnaphthalene	DMF, 0.5 *M* $TBABF_4$/Hg/CV	$E_{1/2}$ = –2.36
1,2-Diphenylnaphthalene	DMF, 0.5 *M* $TBABF_4$/Hg/CV	$E_{1/2}$ = –2.25
Cyclopentanone	DMF, 0.1 *M* TEABr/Hg/pol	$E_{1/2}$ = –2.82
Phenanthrene	MeCN, 0.1 *M* TBAP/Pt wr/CV	$E_{1/2}$ = –2.47
	MeCN, 0.1 *M* TEAP/Hg/pol	$E_{1/2}$ = –2.88[a]
Pentacene	THF, 0.1 *M* TBAP/rot Pt dsk/E swp	$E_{1/2}$ = –1.40
Perylene	MeCN, 0.1 *M* TEAP/Hg/CV	$E_{1/2}$ = –1.73
1,3-Diphenyl-1,3-propanedione	DMSO, 0.2 *M* TBAP/Hg/CV	$E_{1/2}$ = –1.42
2,2-Dimethyl-1,3-diphenyl-1,3 propanedione	DMSO, TBAP/Hg/CV	$E_{1/2}$ = –1.80
Pyrene	DMF, 0.1 *M* TBAP/Pt/CV	E_p = –2.14
	MeCN, 0.1 *M* TEAP/Hg/pol	$E_{1/2}$ = –2.49[a]
Diphenylsulfone	DMF, TEABr	$E_{1/2}$ = –2.16
Triphenylene	MeCN, 0.1 *M* TEAP/Hg/pol	$E_{1/2}$ = –2.87[a]
9,10-Anthraquinone	DMF, 0.5 *M* TBAP, 20°/Pt dsk/CV	$E_{1/2}$ = –1.01
1,4-Benzoquinone	MeCN, 0.1 *M* TEAP/Pt/CV	E_p = –0.54
1,4-Naphthohydroquinone, dipotassium salt	DMF, 0.5 *M* TBAP, 20°/Pt dsk/CV	$E_{1/2}$ = –1.55
Rubrene	DMF, 0.1 *M* TBAP/Pt dsk/CV	E_p = –1.48
	DMF, 0.1 *M* TBAI/Hg/pol	$E_{1/2}$ = –1.410
Benzocyclooctatetraene	THF, 0.1 *M* TBAP/Hg/pol	$E_{1/2}$ = –2.13
sym-Dibenzocyclooctatetraene	THF, 0.1 *M* TBAP/Hg/pol	$E_{1/2}$ = –2.29
Ubiquinone-6	MeCN, 0.1 *M* TEAP/Pt/CV	E_p = –1.05[e]
$(9\text{-Phenyl-fluorenyl})^+$	10.2 *M* H_2SO_4/Hg/CV	E_p = –0.01[b]
$(\text{Triphenylcyclopropenyl})^+$	MeCN, 0.1 *M* TEAP/Hg/CV	E_p = –1.87
$(\text{Triphenylmethyl})^+$	MeCN, 0.1 *M* TBAP/Hg/pol	$E_{1/2}$ = 0.27
	H_2SO_4, 10.2 *M*/Hg/CV	E_p = –0.58[b]
$(\text{Tribiphenylmethyl})^+$	MeCN, 0.1 *M* TBAP/Hg/pol	$E_{1/2}$ = 0.19
$(\text{Tri-4-}t\text{-butyl-5-phenylmethyl})^+$	MeCN, 0.1 *M* TBAP/Hg/pol	$E_{1/2}$ = 0.13
$(\text{Tri-4-isopropylphenylmethyl})^+$	MeCN, 0.1 *M* TBAP/Hg/pol	$E_{1/2}$ = 0.07
$(\text{Tri-4-methylphenylmethyl})^+$	MeCN, 0.1 *M* TBAP/Hg/pol	$E_{1/2}$ = 0.05
$(\text{Tri-4-cyclopropylphenylmethyl})^+$	MeCN, 0.1 *M* TBAP/Hg/pol	$E_{1/2}$ = 0.01
$(\text{Tropylium})^+$	MeCN, 0.1 *M* TBAP/Hg/pol	$E_{1/2}$ = –0.17
	DMF, 0.15 *M* TBAI/Hg/pol	$E_{1/2}$ = –1.55
	DMF, 0.15 *M* TBAI/Hg/pol	$E_{1/2}$ = –1.55
	DMF, 0.15 *M* TBAI/Hg/pol	$E_{1/2}$ = –1.57
	DMF, 0.15 *M* TBAI/Hg/pol	$E_{1/2}$ = –1.60
	DMF, 0.15 *M* TBAI/Hg/pol	$E_{1/2}$ = –1.87
	DMF, 0.15 *M* TBAI/Hg/pol	$E_{1/2}$ = –1.96
	DMF, 0.15 *M* TBAI/Hg/pol	$E_{1/2}$ = –2.05

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REDUCTION AND OXIDATION POTENTIALS FOR CERTAIN ION RADICALS (continued)

Oxidation Potentials (Products are Cation Radicals)

Substance	Conditions/electrode/technique	Potential V (vs. SCE)
Anthracene	CH_2Cl_2, 0.2 *M* $TBABF_4$, –70°C/Pt dsk/CV	E_p = +0.73[d]
9,10-Dimethylanthracene	MeCN, 0.1 *M* $LiClO_4$/Pt wr/CV	E_p = +1.0
9,10-Dipropylanthracene	MeCN, 0.1 *M* TEAP/Pt/CV	E_p = +1.08
1,8-Diphenylanthracene	CH_2Cl_2, 0.2 *M* $TPrACF_3SO_3$/rot Pt wr/E swp	$E_{1/2}$ = +1.34
8,9-Diphenylanthracene	CH_2Cl_2, 0.2 *M* $TPrACF_3SO_3$/rot Pt wr/E swp	$E_{1/2}$ = +1.30
9,10-Diphenylanthracene	MeCN/Pt/CV	E_p = +1.22
Perylene	MeCN, 0.1 *M* TBAP/Pt/CV	E_p = +1.34
Pyrene	DMF, 0.1 *M* TBAP/Pt dsk/CV	E_p = +1.25
Rubrene	DMF, 0.1 *M* TBAP/Pt dsk/CV	E_p = +1.10
Tetracene	CH_2Cl_2, 0.2 *M* $TBABF_4$, –70°C/Pt wr/CV	E_p = +0.35[d]
1,4-Dithiabenzene	MeCN, 0.1 *M* TEAP/Pt dsk/rot	$E_{1/2}$ = +0.69
1,4-Dithianaphthalene	MeCN, 0.1 *M* TEAP/Pt dsk/rot	$E_{1/2}$ = +0.80
Thianthrene	0.1 *M* TPAP/Pt/CV	$E_{1/2}$ = +1.28

[a] vs 0.01 *M* $Ag/AgClO_4$
[b] vs. Hg/Hg_2SO_4, 17 *M* H_2SO_4
[c] vs Hg pool
[d] vs Ag/saturated $AgNO_3$
[e] vs Ag/0.01 *M* Ag^+

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