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**HALF-WAVE POTENTIALS OF
ELECTROACTIVE SUBSTANCES IN
HEXAMETHYLPHOSPHORIC
TRIAMIDE**

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HEXAMETHYLPHOSPHORIC TRIAMIDE

Abstract - After a brief review of the characteristic properties of hexamethylphosphoric triamide as a solvent for electroanalytical use, half-wave potentials of various inorganic and organic electroactive substances in the solvent have been compiled.

Hexamethylphosphoric triamide [tris(dimethylamino)phosphine oxide, hexamethylphosphoramide, hexamethylphosphoric acid triamide, hexametapol; often abbreviated HMPA or HMPT] is a dipolar aprotic solvent with very strong basicity and extremely weak acidity. Some of the physical properties are shown in Table 1. With its characteristic properties, HMPA has been used in various fields of chemistry[ref. 1]. It is also interesting as a solvent for electroanalytical chemistry, and methods for its purification and test of purity have been reviewed from this standpoint[ref. 2].

HMPA is fairly stable to electrochemical reduction, but is not stable against anodic oxidation. In anhydrous HMPA containing 0.2M NaClO_4 ($M = \text{mol dm}^{-3}$), the useful potential range at a platinum electrode extends from +0.7 to -3.3V vs. an $\text{Ag}/0.1\text{M AgClO}_4$ (HMPA) reference electrode (hereafter abbreviated Ag/Ag^+). The cathodic potential limit is determined by the dissolution of electrons from the electrode, while the anodic potential limit is due to the oxidation of the solvent. Solvated electrons are stable in this solution even at room temperatures. Electrochemistry of solvated electrons has been studied extensively in HMPA[ref. 3]. The formal potential for the reaction $e^-(\text{solvent}) \rightleftharpoons e^-(\text{Pt-metal})$ in HMPA-0.2M NaClO_4 has been determined to be -3.44V vs. Ag/Ag^+ at 5 °C[ref. 4]. In 0.2M tetrabutylammonium perchlorate (TBAP), the potential range at a platinum electrode is also from +0.7 to -3.3V vs. Ag/Ag^+ , but solvated electrons are not generated[ref. 4]. The potential range at a dropping mercury electrode (DME) is from -0.2 to -3.2V vs. Ag/Ag^+ in 0.05M tetrahexylammonium perchlorate (THAP), to -3.1V in 0.05M TBAP and tetraheptylammonium perchlorate (THpAP), to -3.0V in 0.05M tetraethylammonium perchlorate (TEAP), and to -2.7V in 0.05M LiClO_4 [ref. 5]. Solvated electrons are not generated at a mercury electrode. (For more details of the potential range, see ref. 13.)

Metal ions are solvated strongly in HMPA, and well-defined, reversible reduction waves can be obtained only for several metal ions. The reductions of metal ions at more negative potentials, especially those of alkali and alkaline earth metal ions, are influenced significantly by the cation of the supporting electrolyte[refs. 6-11]. As an example, reduction waves of sodium ions at a DME are shown in Fig. 1. Sodium ions do not give a reduction wave in 0.05M TEAP. In 0.05M TBAP or THAP, a reduction wave is observed but it is kinetically controlled and is smaller than that expected for a diffusion controlled process. In 0.05M THpAP or LiClO_4 , the sodium wave becomes nearly reversible and diffusion controlled. This marked effect of the cation of the supporting electrolyte has been interpreted by means of the double layer ef-

Table 1. Physical properties of HMPA, $[(\text{CH}_3)_2\text{N}]_3\text{P}=\text{O}$ [ref. 2]

Freezing temp.		7.2 °C
Boiling temp.	760 mmHg	233 °C
	15 mmHg	115 °C
	1 mmHg	68-70 °C
Density, 25 °C		1.020 g cm ⁻³
Viscosity, 25 °C		3.25 cP
Relative permittivity,		
	25 °C	29.6
Dipole moment μ , 25 °C		
	liquid HMPA	5.38 D
Donor number		38.8
Acceptor number		10.6

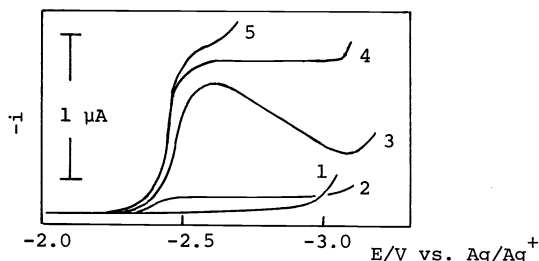


Fig. 1. Effect of the cation of the supporting electrolyte on the reduction wave of 1mM sodium ion in HMPA. (Supporting electrolyte: curve 1, tetraethylammonium perchlorate; 2, tetrabutylammonium perchlorate; 3, tetrahexylammonium perchlorate; 4, tetraheptylammonium perchlorate; and 5, LiClO_4 . Each in 0.05 M)

fect which takes into account relative locations of the outer Helmholtz plane and the plane of the charge centers of reactive species [refs. 7,12]. In HMPA the size of solvated cations, determined by a conductometric method, is in the following order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+, \text{Rb}^+, \text{Cs}^+ > \text{Me}_4\text{N}^+ > \text{Et}_4\text{N}^+ < \text{Pr}_4\text{N}^+ < \text{Bu}_4\text{N}^+ < \text{Hex}_4\text{N}^+, \text{Hep}_4\text{N}^+$. In general, the reduction of heavily solvated metal ions at negative potentials are most difficult in the supporting electrolyte containing tetraethylammonium ions, the smallest cation in HMPA, and becomes easier and more reversible with the increase of the cationic size of the supporting electrolyte. Unfortunately, however, reduction waves in the supporting electrolyte of larger cations are often accompanied by a big polarographic maximum. Univalent radical anions in HMPA are more stable than in other popular aprotic solvents. Thus, the first reduction waves of many organic compounds and dissolved oxygen are one-electron processes to form such anions.

HMPA containing dissolved oxygen is unstable and its peroxide ($[(\text{CH}_3)_2\text{N}]_2[(\text{CH}_3)(\text{CH}_2\text{OOH})\text{N}]\text{P}=\text{O}$) is formed on exposure to light. The peroxide gives a reduction wave of $E_{1/2}$ equal to -1.81V vs. Ag/Ag^+ at a DME in 0.1M TEAP [ref. 13]. Purified HMPA should be kept in the dark under an inert atmosphere or under vacuum and used soon after the purification [ref. 2]. Warning has been reported that malignant tumors have been produced in laboratory animals by exposure to HMPA [ref. 14]. Experiments using HMPA should be carried out with great care.

In Tables 2, 3 and 4, half-wave potentials of various inorganic and organic electroactive substances are listed. In these tables, unless otherwise stated, Ag/Ag^+ shows the $\text{Ag}/0.1\text{M AgClO}_4$ (HMPA) electrode. The potential of the electrode is $+0.36\text{V}$ vs. aqueous SCE, when both electrodes are immersed in HMPA-0.05M TEAP. This potential, of course, includes a liquid junction potential between different solvents, which may change to a considerable extent by the change of the electrolyte compositions at the boundary. The potential of the Ag/Ag^+ electrode is -0.22_5V vs. the standard potential of ferrocene/ferrocinium ion (Fc/Fc^+) electrode [ref. 15], and the potential of the bisbiphenylchromium(0)/bisbiphenylchromium(I) ion (BCr/BCr^+) system in 0.1M TBAP is -1.12V vs. Fc/Fc^+ electrode [ref. 32]. In the tables, comments on the reversibilities of the waves were added after the values of half-wave potentials. They were checked in most cases by dc polarographic wave analyses, but in some cases by ac polarography or by cyclic voltammetry. They should be taken as more or less qualitative.

Table 2. Half-wave potentials of reductions of inorganic substances (25 °C)

Electroactive substance (Indicator electrode) *1	Supporting electrolyte *2	Reference electrode *3	$E_{1/2}$ (V); n; and other remarks *4	Ref.
H ⁺ (DME)	0.05M TBAP	A	-1.8 ₁ (1 mM); irrev.	10)
H ⁺ (RPPE)	0.5M NaClO ₄	Ag/0.01M Ag ⁺	-0.85 (1 mM); 1; 2H ⁺ → H ₂	15)
Li ⁺ (DME)	0.05M TEAP	A	N.R.	7)
	0.1M TEAP	B	N.R.	17)
	0.05M TBAP	A	N.R.	7)
	0.05M THAP	A	N.R.	11)
	0.05M LiClO ₄	A	redn. of Li ⁺ starts from -2.65V	7)
Na ⁺ (DME)	0.05M TEAP	A	N.R.	7)
	0.1M TEAP	B	N.R.	17)
	0.05M TBAP	A	-2.42; <u>a</u>	7)
	0.05M THAP	A	-2.49; <u>a</u>	11)
	0.05M THpAP	A	-2.47; 1; rev.	11)
K ⁺ (DME)	0.05M LiClO ₄	A	-2.47; 1; rev.	7)
	0.05M TEAP	A	-2.37; <u>a</u>	7)
	0.1M TEAP	B	-2.09; s=120 mV	17)
	0.05M TBAP	A	-2.38; 1; rev.	7)
	0.05M THAP	A	-2.39; 1; rev.	11)
Rb ⁺ (DME)	0.05M LiClO ₄	A	-2.37; 1; rev.	7)
	0.05M TEAP	A	-2.35; 1; rev.	7)
	0.1M TEAP	B	-2.043; s=92 mV	17)
Cs ⁺ (DME)	0.05M TBAP	A	-2.35; 1; rev.	7)
	0.05M LiClO ₄	A	(-2.35); 1; <u>b</u>	7)
	0.05M TEAP	A	-2.32; 1; rev.	7)
NH ₄ ⁺ (DME)	0.1M TEAP	B	-1.981; s=80 mV	17)
	0.05M LiClO ₄	A	(-2.32); 1; <u>b</u>	7)
	0.05M TEAP	A	-2.48; irrev., <u>a</u>	21)
Tl ⁺ (DME)	0.05M TBAP	A	-2.31; 1; irrev.	21)
	0.05M TEAP	A	-0.83; 1; near rev.	10)
	0.05M TBAP	A	-0.83; 1; near rev.	10)
Ca ²⁺ (DME)	0.05M LiClO ₄	A	-0.83; 1; near rev.	10)
	0.05M TEAP	A	N.R.	8)
	0.05M TBAP	A	-2.82; irrev., <u>a</u>	8)
Sr ²⁺ (DME)	0.05M THAP	A	(-2.76); 2; <u>b</u>	8)
	0.05M TEAP	A	N.R.	8)
	0.05M TBAP	A	-2.70; irrev., <u>a</u>	8)
Ba ²⁺ (DME)	0.05M THAP	A	(-2.6 ₁); 2; <u>b</u>	8)
	0.05M TEAP	A	N.R.	8)
	0.1M TEAP	B	N.R.	17)
	0.05M TBAP	A	-2.45; irrev., <u>a</u>	8)
	0.05M THAP	A	(-2.4 ₁); 2; <u>b</u>	8)
	0.05M LiClO ₄	A	(-2.4 ₀); 2; <u>b</u>	8)

Table 2 (continued)

Electroactive substance (Indicator electrode) *1	Supporting electrolyte *2	Reference electrode *3	$E_{1/2}$ (V); n; and other remarks *4	Ref.
Cu ²⁺ (DME)	0.05M TEAP	A	2nd wave: -0.45	10)
	0.1M TEAP	B	1st wave: more positive than the dissolution of mercury, 2nd wave: -0.08; 1; rev.	20)
Cu ²⁺ (RPE)	0.1M TEAP	B	1st wave: +0.30; 1; near rev., 2nd wave: -0.35; 1; near rev.	20)
[CuN ₂ S ₂] (Pt-wire) *5	0.1M TBAP	BCr/BCr ⁺	-0.446; 1; near rev.	29)
Cd ²⁺ (DME)	0.1M TEAP	B	-0.531; 2; rev.	17)
Pb ²⁺ (DME)	0.1M TEAP	B	wave, with a prewave and a polarogr. maximum, starts at ca. -0.5V	17)
Co ²⁺ (DME)	0.05M TEAP	A	ill-defined wave between -1.3 and -2.0V, <u>a</u>	10)
	0.05M TBAP	A	wave with a big polarogr. maximum between -1.5 and -2.0V	10)
Ni ²⁺ (DME)	0.05M TEAP, TBAP, or LiClO ₄	A	wave with a big polarogr. maximum between -1.0 and -1.2V	10)
Zn ²⁺ (DME)	0.05M TEAP	A	-1.8; irrev., <u>a</u>	10)
	0.05M TBAP or LiClO ₄	A	wave with a big polarogr. maximum between -1.6 and -2.2V; wave-height proportional to concn.	10)
[Co(en) ₃] ³⁺ (DME)	0.1M TEAP	BCr/BCr ⁺	+0.125 (+0.11); 1; rev.	22,23)
Fe ³⁺ (DME)	0.05M TEAP	A	1st wave: -0.88; <u>a</u> 2nd wave: -1.87; <u>a</u>	10)
	0.05M TBAP	A	1st wave: -0.85, 2nd wave: (-1.8 ₃); with a maximum	10)
I ₂ (DME)	0.05M TEAP	A	1st wave: -0.33; 2/3; rev., *6 2nd wave: -0.78; 4/3; rev., *6	27)
O ₂ (DME)	0.05M TEAP	A	1st wave: -1.32; 1; O ₂ → O ₂ ⁻ , rev., 2nd wave: -1.89; irrev.	18)
	0.05M TBAP	A	1st wave: -1.32; 1; O ₂ → O ₂ ⁻ , rev., 2nd wave: -2.35; irrev.	18)
	0.05M THAP	A	1st wave: -1.33; 1; O ₂ → O ₂ ⁻ , rev., 2nd wave does not appear.	18)
	0.05M LiClO ₄	A	1st wave: (-1.36); with a polarogr. maximum, 2nd wave: -1.92	18)
	0.05M CsClO ₄	A	1st wave; -1.17, 2nd wave: -1.52, 3rd wave: -1.86	18)
H ₂ O ₂ (DME)	0.1M TEAP	A	-2.32	19)
	0.1M LiClO ₄	A	-2.13	19)
SO ₂ (DME)	0.1M TEAP	Ag/0.05M AgNO ₃ +0.05M TEAP	-1.16; *7	28)

Notes to Table 2:

*1 All metal ions were added as perchlorates. DME, dropping mercury electrode; RPE, rotated platinum electrode; and RPPE, rotated platinized platinum electrode.

*2 TEAP, tetraethylammonium perchlorate; TBAP, tetrabutylammonium perchlorate; THAP, tetrahexylammonium perchlorate; and THpAP, tetraheptylammonium perchlorate.

*3 'A' stands for an Ag/0.1M AgClO₄ electrode in HMPA, and 'B' an aqueous SCE. For the relative potentials of the reference electrodes, see text.

Notes to Table 2 (continued):

- *4 $E_{1/2}$ values in parentheses are for waves with a polarographic maximum and are not reliable. 'n' is the number of electrons and shown only when it is available. Rev., reversible; and irrev., irreversible. N.R. means that no reduction wave was observed before the reduction of the supporting electrolyte. 'a', a wave with a more or less kinetically controlled wave-height; 'b', a wave with a polarographic maximum but with a diffusion controlled limiting current; and 's', the slope of a plot of E vs. $\log[(i_d - i)/i]$.
- *5 $[\text{CuN}_2\text{S}_2] = \text{N,N}'\text{-ethylenebis(thioacetylacetoniminato)copper(II)}$. It is reduced to $[\text{CuN}_2\text{S}_2]^-$ and oxidized to $[\text{CuN}_2\text{S}_2]^+$. $E_{1/2} = (E_{pc} + E_{pa})/2$ in cyclic voltammetry.
- *6 1st wave: $\text{I}_2 + \text{Hg} \rightarrow \text{HgI}_2$, $3\text{HgI}_2 + 2e \rightleftharpoons 2\text{HgI}_3^- + \text{Hg}$,
2nd wave: $2\text{HgI}_3^- + 4e \rightleftharpoons 6\text{I}^- + 2\text{Hg}$
- *7 $\text{SO}_2 + e \rightleftharpoons \text{SO}_2^-$, $2\text{SO}_2^- \rightleftharpoons \text{SO} + \text{SO}_3^{2-}$, $K_d = [\text{SO}][\text{SO}_3^{2-}]/[\text{SO}_2^-]^2 = 1.5$.
- *8 $E_{1/2}$ of the following nickel complexes at a DME have been measured in 0.2M TBAP against Ag-wire electrode[ref. 31]: $\text{Ni}(\text{bpy})_2$, $\text{Ni}(\text{AN})_2(\text{bpy})$, $\text{Ni}(\text{FN})_2(\text{bpy})$, $\text{Ni}(\text{AN})_2$, and $\text{Ni}(\text{FN})_2$, where bpy, AN and FN show 2,2'-bipyridyl, acrylonitrile and fumaronitrile, respectively.

Table 3. Half-wave potentials of oxidations of inorganic substances (25 °C)^{*1}

Electroactive substance (Indicator electrode)	Supporting electrolyte	Reference electrode	$E_{1/2}$ (V) and remarks	Ref.
Cl^- (DME)	0.1M TEAP	B	1st wave: -0.328, 2nd wave: +0.095; *2	17)
Br^- (DME)	0.1M TEAP	B	drawn out wave(s), *2	17)
I^- (DME) 1.39 mM	0.1M TEAP	B	1st wave: -0.322, 2nd wave: +0.046; *2	17)
I^- (RPE) 1.04 mM	0.1M TEAP	B	1st wave: +0.371, 2nd wave: +0.818; *3	17)
0.104 mM			1st wave: +0.351, 2nd wave: +0.717; *3	
0.041 mM			1st wave: +0.347, 2nd wave: +0.504; *3	
H_2 (RPPE)	0.5M NaClO_4	Ag/0.01M Ag^+	-0.80; n = 2	15)
$[\text{CuN}_2\text{S}_2]$ (Pt-wire)	0.1M TBAP	BCr/BCr ⁺	+1.051; n = 1, rev., *4	29)
$[\text{cis}(\text{imidine})_2\text{Cr}(\text{CO})_4]$ (Pt) ^{*5}	0.1M TBAP	BCr/BCr ⁺	+0.88; n = 1, near rev.	16)

Notes to Table 3:

- *1 See Notes *1 - *4 of Table 2.
- *2 The product of the first wave seems to be HgX_3^- , and that of the second wave HgX_2 (X^- : Cl^- , Br^- or I^-).
- *3 The product of the first wave is I_3^- , and that of the second wave I_2 .
- *4 See Note *5 of Table 2.
- *5 $[\text{cis}(\text{imidine})_2\text{Cr}(\text{CO})_4] = \text{cis-tetracarbonyl-bis}(1,3\text{-dimethylimidazolidin-2-ylidene})\text{-chromium}(0)$. It is oxidized to $[\text{cis}(\text{imidine})_2\text{Cr}(\text{CO})_4]^+$. $E_{1/2} = (E_{pc} + E_{pa})/2$.

Table 4. Half-wave potentials of reductions of organic substances (25 °C) *1

Electroactive substance (Indicator electrode) *2	Supporting electrolyte *3	Reference electrode *4	$E_{1/2}$ (V); n; and other remarks *5	Ref.
BDTA ⁺ (DME) *6	0.05M TEAP	A	-2.57; s=87 mV, a	21)
	0.05M TBAP	A	-2.45; s=77 mV	21)
(Decyl) ₄ N ⁺ (DME)	0.05M TEAP	A	-1.98; irrev., s=338 mV	21)
	0.05M TBAP	A	-2.24; irrev., s=330 mV	21)
(Dodecyl) ₄ N ⁺ (DME)	0.05M TEAP	A	-2.03; irrev., s=280 mV	21)
	0.05M TBAP	A	-2.23; irrev., s=250 mV	21)
	0.05M LiClO ₄	A	-2.10; irrev., s=180 mV	21)
Anthracene (GC disc) *7	0.1M TEAP	Li/sat. LiCl	1st wave: +1.26; 1; rev., 2nd wave: +0.58(E _p); irrev., anodic wave in c.v.: +1.95(E _p)	24)
	0.1M TBAP	Li/sat. LiCl	1st wave: +1.25; 1; rev., 2nd wave: +0.47(E _p), irrev., anodic wave in c.v.: +1.89(E _p)	24)
	0.3M LiCl	Li/sat. LiCl	1st wave: +1.26; 1; rev., 2nd wave: +0.33(E _p), irrev.	24)
9,10-Anthraquinone (DME)	0.1M TEAP	Fc/Fc ⁺	1st wave: -1.48; 1; rev.	30)
Azobenzene (HMDE)	sat. LiCl	B	1st wave: -1.30; 1; rev., 2nd wave does not appear.	26)
1,1 - Diphenylethylene (HMDE)	Bu ₄ NBF ₄	B	1st wave: -2.42(E _p); irrev.	25)
α-Methylstilbene (HMDE)	Bu ₄ NBF ₄	B	1st wave: -2.18; 1; rev., 2nd wave: -2.58(E _p); irrev.	25)
Nitrobenzene (GC disc)	0.1M TEAP	Li/sat. LiCl	1st wave: +1.93(E _p); 1; rev., 2nd wave: +1.18(E _p); 1	24)
	0.3M LiCl	Li/sat. LiCl	1st wave: +1.99(E _p); 1; rev., 2nd wave: +1.20(E _p); 1	24)
9,10-Phenanthrenequinone (HMDE)	0.1M TEAP	Fc/Fc ⁺	1st wave: -1.24; 1; rev.	30)
trans-Stilbene (HMDE)	Bu ₄ NBF ₄	B	1st wave: -2.11; 1; rev., 2nd wave: -2.65(E _p); irrev.	25)
Tetraphenylethylene (HMDE)	Bu ₄ NBF ₄	B	1st wave: -1.97; 1; rev., 2nd wave: -2.17; rev.	25)
	sat. LiCl	B	1st wave: -1.91; 1; rev., 2nd wave: -2.13(E _p); rev.	25)
Triphenylethylene (HMDE)	Bu ₄ NBF ₄	B	1st wave: -2.05; 1; rev., 2nd wave: -2.43(E _p); irrev.	25)
	sat. LiCl	B	1st wave: -1.95; 1; rev., 2nd wave: -2.3(E _p); irrev.	25)

Notes to Table 4:

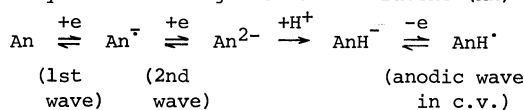
*1 See Notes *1 - *4 of Table 2.

*2 GC disc, glassy carbon disc electrode; and HMDE, hanging mercury drop electrode.

*3 Concentration of Bu₄NBF₄ not given.*4 The potential of Li/sat. LiCl (HMPA) electrode is -3.21V vs. aq. SCE. (L. A. Avaca and A. Bewick, *J. Electroanal. Chem.*, **41**, 395 (1973))*5 For many of the uncharged electroactive substances, measurements were carried out by cyclic voltammetry (c.v.). Values accompanied by (E_p) show peak potentials, while those not accompanied by (E_p) show (E_{pc} + E_{pa})/2. The first waves for all of the uncharged substances correspond to 1-electron processes to form radical anions.*6 BDTA⁺ = benzyldimethyl(tetradecyl)ammonium ion.

Notes to Table 4 (continued):

*7 The cyclic voltammograms for anthracene (An) fit the following scheme:



*8 $E_{1/2}$ for the two reduction waves of 2,2'-bipyridyl are -2.37 and -2.80V, respectively, against Ag-wire electrode in 0.2M TBAP [ref. 31].

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