



Electrochemistry

CHEM 5390

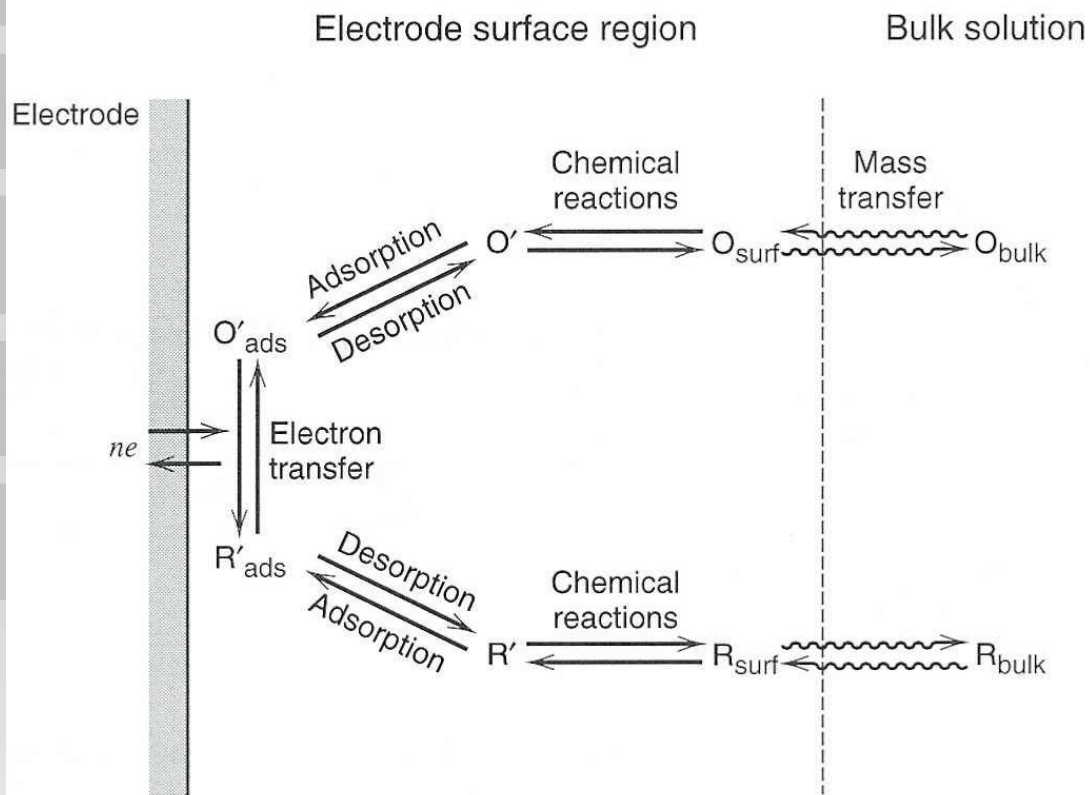


Figure 1.3.6 Pathway of a general electrode reaction.

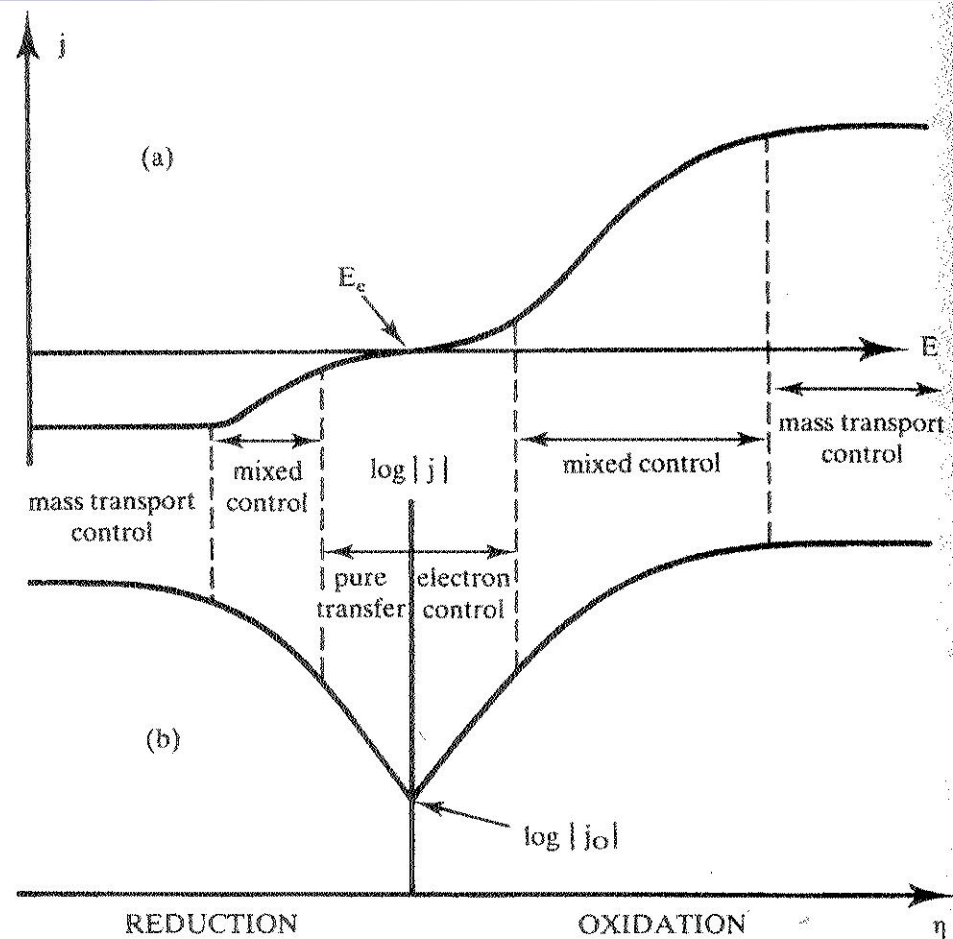


Figure 1.14 $j - E$ response and the corresponding $\log j - \eta$ curve for an irreversible electrode reaction $O + e^- = R$. $c_R = 10c_O$.

Organic Electrochemistry

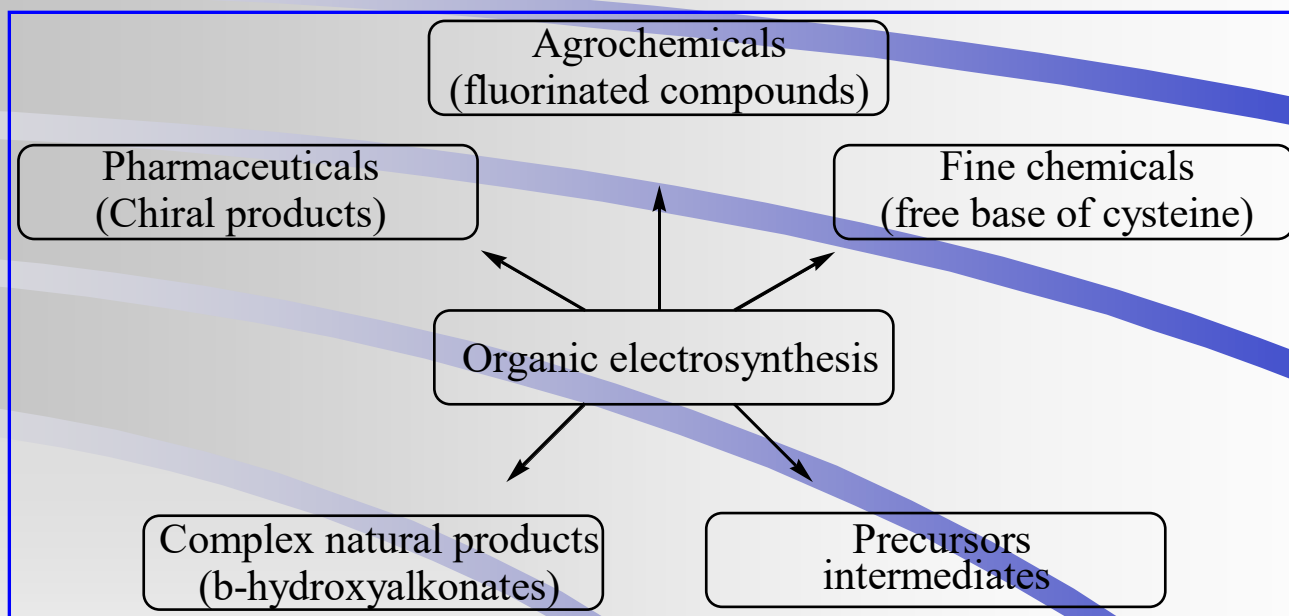
Organic Electrochemistry is a multidisciplinary science overlapping the fields of organic chemistry, biochemistry, physical chemistry and electrochemistry.

The first electroorganic synthesis was performed by Michael Faraday (1843), the anodic decarboxylation of acetic acid, and the formation of ethane via creation of a new carbon-carbon bond:



Organic Electrochemistry

Organic electrosynthesis



Organic Electrochemistry

Many organic reactions are Lewis acid-base processes that involve the interaction of a nucleophilic center with an electrophilic center.

Nucleophile (Lewis base) donates electrons and electrophile (Lewis acid) accepts electrons

Electrochemistry provides the electrons needed for these reactions.

Organic Electrochemistry

Electrochemistry provides the electrons needed for these reactions.

The cathode acts as the ultimate nucleophile and the anode as the electrophile.

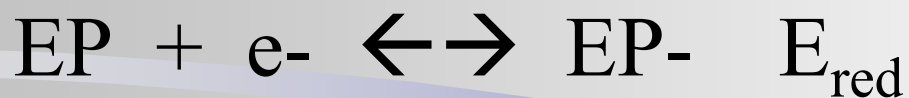
Organic Electrochemistry

Carbon centers (saturated hydrocarbons) are resistant to electrochemical reduction or oxidation.

Organic molecules with electrophilic components (alkyl-, aryl-, acyl-halides; carbonyl groups, unsaturated and aromatic hydrocarbons, nitro groups) react with the solvated electron (nucleophile).

Organic Electrochemistry

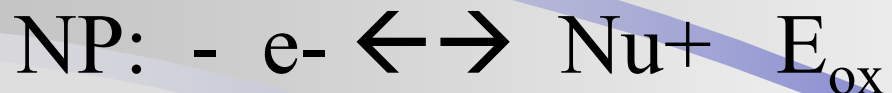
The reduction potential, E_{red} , is a measure of the molecules electron affinity.



More positive the potential the more electrophilic the molecule.

Organic Electrochemistry

Organic molecules with nucleophilic components (catechols, hydroquinones, phenols, alcohols, thiols, aromatic hydrocarbons, and amines) can be oxidized.



The more negative the potential the more nucleophilic the molecule.

Organic Electrochemistry

TABLE 1.3 Nucleophilicity and Electrophilicity of Molecules and Ions^a

Nucleophile	$(E_{1/2})_{\text{ox}}$, V vs. NHE		Electrophile	$(E_{1/2})_{\text{red}}$, V vs. NHE	
	(MeCN)	(H ₂ O)		(MeCN)	(H ₂ O)
e_{aq}^-	-3.9	-2.9	H ₂ O ⁺ ·	+3.2	+2.7
K·	-2.9	-2.9	Ph ⁺ ·CH ₂ OH	+2.2	
Na·	-2.1	-2.7	Au ⁺	+1.6	+1.8
Li·	-2.0		(Cl ₈ TPP ⁺ ·)Fe ^{IV} =O	+1.5	
(TPP ⁻ ·)Co ⁻	-1.7		(compound I)		
H·	-1.6	-2.1	Fe ^{III} (bpy) ₃ ³⁺	+1.3	+1.1
(TPP ⁻ ·)Fe ⁻	-1.4		HO·	+0.9	+1.9
(TPP)Fe ⁻	-0.8		Fe ^{III} (PA) ₃	+0.4	
(TPP)Co ⁻	-0.6		(TPP)Fe ^{III} (py) ₂ ⁺	+0.4	
O ₂ ⁻ ·	-0.7	-0.2	(TPP)Fe ^{III} Cl	+0.2	
PhCH ₂ S ⁻	0.0		MV ²⁺	-0.2	
HOO ⁻	0.0	+0.7	(Cl ₈ TPP)Fe ^{IV} =O	-0.3	
PhO ⁻	+0.3		(compound II)		
Me ₃ N	+0.7		AQ (anthraquinone)	-0.6	
HO ⁻	+0.9	+1.9	O ₂	-0.7	-0.2
MeC(O)O ⁻	+1.5		CCl ₄	-0.9	
PhOH	+1.7		PhCH ₂ Br	-1.4	
pyridine	+2.0		PhCl ₆	-1.4	
Cl ⁻	+2.2	+2.4	H ₃ O ⁺	-1.6	-2.1
HOOH	+2.3	+1.0	<i>t</i> -BuI	-1.5	
H ₂ O	+3.0	+2.3	PhCH ₂ Cl	-1.7	
			<i>n</i> -BuI	-1.9	
			<i>c</i> -C ₆ H ₁₁ Br	-1.9	
			<i>t</i> -BuBr	-2.0	
			<i>n</i> -BuBr	-2.2	
			<i>n</i> -BuCl	-2.5	
			PhCl	-2.6	
			H ₂ O	-3.9	-2.9

^aStrongest or most reactive at top of listing.

Organic Electrochemistry

Example of electrophilic reaction (halo-groups)

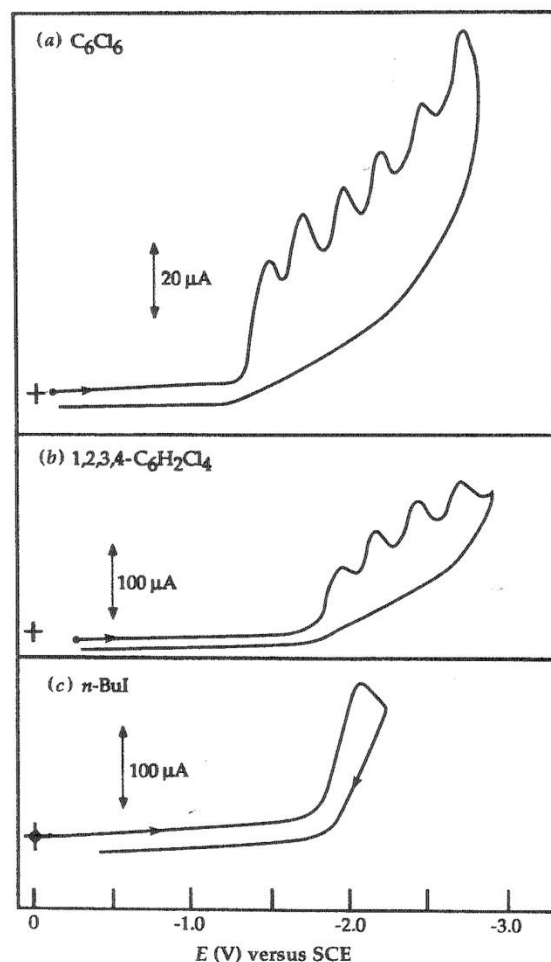
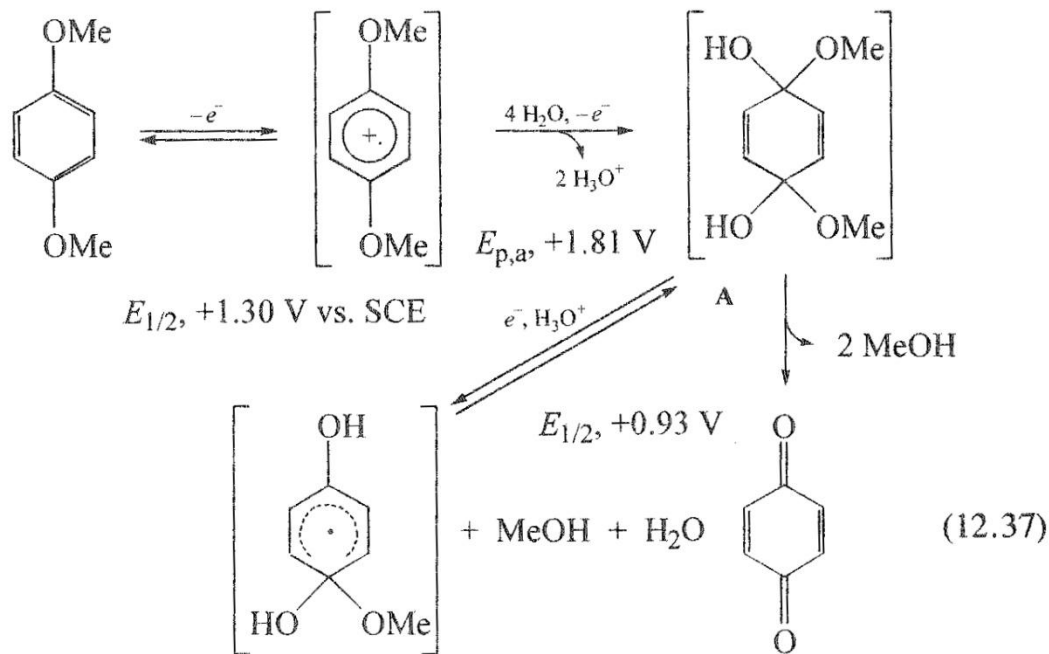


Figure 12.1 Cyclic voltammograms for chlorinated aromatic molecules and *n*-butyl iodide in dimethylformamide (0.1 M TEAP) at a glassy-carbon electrode (area 0.062 cm²): (a) 1.1 mM C_6Cl_6 ; (b) 2.3 mM 1,2,3,4- $C_6H_2Cl_4$; (c) 20 mM *n*-BuI.

Organic Electrochemistry

Example of nucleophilic reaction (ring can delocalize the charge).



Organic Electrochemistry

Example of nucleophilic reaction (ring can delocalize the charge).

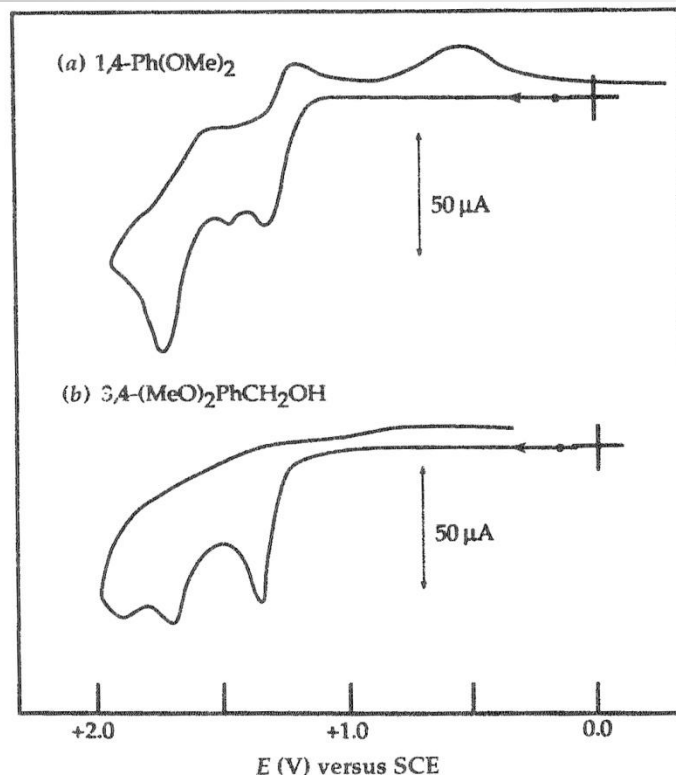


Figure 12.5 Cyclic voltammograms of (a) 1.5 mM 1,4- $\text{Ph}(\text{OMe})_2$ and (b) 3,4- $(\text{MeO})_2\text{PhCH}_2\text{OH}$ in MeCN [0.1 M $(\text{Et}_4\text{N})\text{ClO}_4$]. Scan rate 0.1 V s^{-1} ; GCE (0.09 cm^2); SCE versus NHE, + 0.244 V.

Organic Electrochemistry

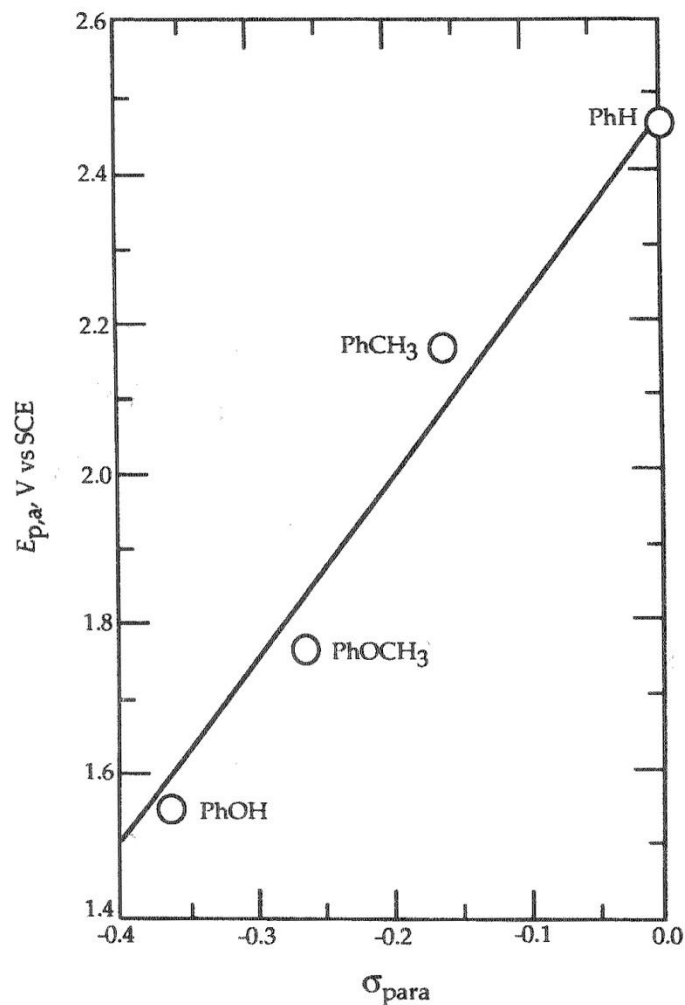


Figure 12.6 Voltammetric oxidation potentials ($E_{p,a}$) of substituted benzenes versus their substituent constants (σ_{para} , Ref. 16); slope, $2.43 \text{ V } \sigma^{-1}$. Conditions: 1 mM substrate in MeCN [0.1 M $(\text{Et}_4\text{N})\text{ClO}_4$]; scan rate 0.1 V s^{-1} ; GCE (0.09 cm^2) (Ref. 18).

Organic Electrochemistry

Non-aqueous Solvents

Solvents other than water are generally organic solvents (although recently ionic liquids have been introduced).

Organic Electrochemistry

Non-aqueous Solvents

Properties to consider:

- Boiling point
- Toxicity
- Viscosity (influences rate of mass transfer)
- Relative permittivity, ϵ_r (influences electrostatic interactions between electric charges) $\epsilon_r > 15$ are polar
- Acidity (ability to accept electrons and donate protons)
- Basicity (ability to donate electrons and accept protons)

Organic Electrochemistry

Tab. 1.2 Physical and chemical properties of solvents

Physical properties	<i>Bulk properties:</i> boiling point, melting (or freezing) point, molar mass, density, viscosity, vapor pressure, heat capacity, heat of vaporization, refractive index, relative permittivity, electric conductivity; <i>Molecular properties:</i> dipole moment, polarizability
Chemical properties	Acidity (including the abilities as proton donor, hydrogen-bond donor, electron pair acceptor, and electron acceptor) ¹⁾ ; Basicity (including the abilities as proton acceptor, hydrogen-bond acceptor, electron pair donor, and electron donor) ¹⁾

1) The terms 'acidity' and 'basicity' are used in somewhat wider ways than usual (see text).

Organic Electrochemistry

DN – basicity scale AN – acidity scale

Tab. 1.5 Chemical properties of organic solvents of electrochemical interest. Donor numbers (DN), acceptor numbers (AN), and autoprotolysis constants (pK_{SH}) [with relative permittivities (ϵ_r)]

Solvent ¹⁾	DN	AN	pK_{SH}	ϵ_r	Solvent	DN	AN	pK_{SH}	ϵ_r
47) 1,2-Dichloroethane (DCE)	0	16.7		10.4	6) Methanol (MeOH)	(19)	41.3	17.2	32.7
41) Hexane	(0)	0		1.88	3) Formic acid	(19)	83.6	6.2	58.5 ₁₆
42) Benzene	0.1	8.2		2.27	12) Tetrahydrofuran (THF)	20.0	8.0		7.6
44) Nitromethane (NM)	2.7	20.5		36.7	4) Acetic acid (HOAc)	(20)	52.9	14.45	6.2
45) Nitrobenzene (NB)	4.4	14.8		34.8	14) 1,2-Dimethoxyethane (DME)	23.9	10.2		7.2
5) Acetic anhydride	10.5	–	14.5	20.7 ₁₉	27) Formamide (FA)	(24)	39.8	16.8 ₂₀	111.0
23) Benzonitrile (BN)	12.0	–		25.2	29) <i>N,N</i> -Dimethylformamide (DMF)	26.6	16.0	29.4	36.7
19) Acetonitrile (AN)	14.1	18.9	33.3	35.9	34) <i>N</i> -Methyl-2-pyrrolidinone (NMP)	27.3	13.3	25.6	32.2
38) Sulfolane (TMS)	14.8	–	25.5	43.3	31) <i>N,N</i> -Dimethylacetamide (DMA)	27.8	13.6	23.9	37.8
13) 1,4-Dioxane	14.8	10.8		2.21	35) Tetramethylurea (TMU)	29.6			23.6
49) Propylene carbonate (PC)	15.1	18.3		66.1	37) Dimethyl sulfoxide (DMSO)	29.8	19.3	33.3	46.5
Diethyl carbonate (DEC)	16.0	–		2.8	26) Pyridine (Py)	33.1	14.2		12.9
50) Ethylene carbonate (EC)	16.4	–		89.6	33) Hexamethylphosphoric triamide (HMPA)	38.8	10.6	20.6	29.6
51) Methyl acetate (MA)	16.5	10.7		6.7	7) Ethanol (EtOH)	(32?)	37.9	19.1	24.6
21) Butyronitrile (BuN)	16.6	–		20.3	8) 1-Propanol (1-PrOH)		37.3	19.4	20.5
16) Acetone (Ac)	17.0	12.5	32.5	20.7	9) 2-Propanol (2-PrOH)	(36?)	33.6	21.1	19.9
52) Ethyl acetate	17.1	9.3	22.8	6.0	28) <i>N</i> -Methylformamide (NMF)	(49?)	32.1	10.74	182.4
48) γ -Butyrolactone (γ -BL)	(18)	17.3		39	Trifluoroacetic acid		105.3		8.55
1) (Water)	18(G)– 33(L) ²⁾	54.8	14.0	78.4					

1) For the numbers before the solvent names, see Tab.1.1.

2) G means gas and L means liquid.

Organic Electrochemistry

Tab. 1.7 Acid-base properties of solvents and the characteristics of reactions

<i>Solvents with weak (strong) acidity</i>	<i>Solvents with weak (strong) basicity</i>
1) Solvation to small anions is difficult (easy) <ul style="list-style-type: none">• Small anions are reactive (not reactive)	1) Solvation to small cations is difficult (easy) <ul style="list-style-type: none">• Small cations are reactive (not reactive)
2) Proton donation from solvent is difficult (easy) <ul style="list-style-type: none">• pH region is wide (narrow) on the basic side• Strong bases are differentiated (leveled)• Very weak acids can (cannot) be titrated	2) Proton acceptance by solvent is difficult (easy) <ul style="list-style-type: none">• pH region is wide (narrow) on the acidic side• Strong acids are differentiated (leveled)• Very weak bases can (cannot) be titrated
3) Reduction of solvent is difficult (easy) <ul style="list-style-type: none">• Potential region is wide (narrow) on negative side• Strong reducing agent is stable (unstable) in the solvent• Substances difficult to reduce can (cannot) be reduced	3) Oxidation of solvent is difficult (easy) <ul style="list-style-type: none">• Potential region is wide (narrow) on positive side• Strong oxidizing agent is stable (unstable) in the solvent• Substances difficult to oxidize can (cannot) be oxidized

Organic Electrochemistry

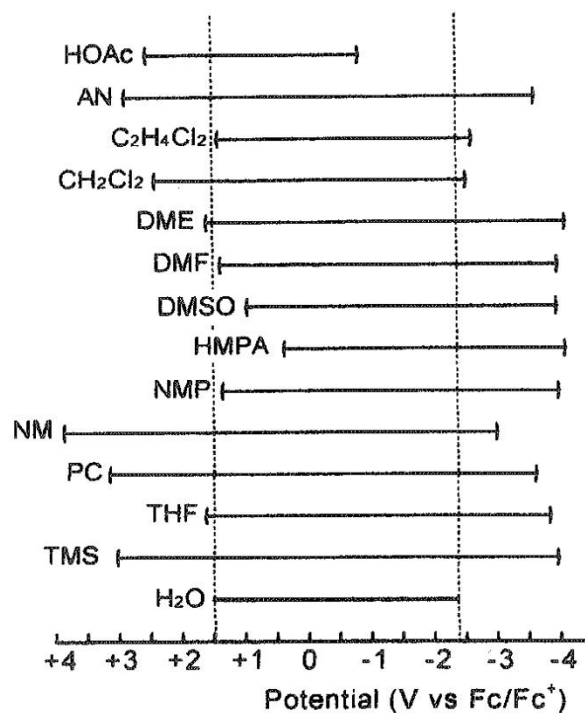
Non-aqueous Solvents

Potential window (electrochemical window) are convenient to predict the usefulness of solvents for redox reactions.

Organic Electrochemistry

Non-aqueous Solvents

Fig. 4.8 Potential windows in various solvents based on a common potential scale (vs Fc^+/Fc). Obtained by voltammetry at a smooth Pt electrode at $10\mu\text{Amm}^{-2}$.



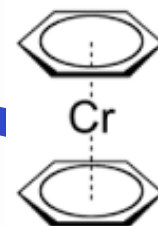
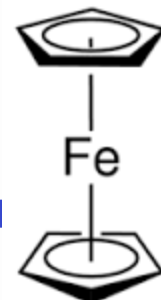
Organic Electrochemistry

Since there is no reliable reference electrode for non-aqueous solutions, IUPAC has developed a method for reporting electrode potentials.

Organic Electrochemistry

IUPAC method

- Ferrocene Fc^+/Fc or bis(biphenyl)chromium BCr^+/BCr are used as reference redox system.
- Potential of the reference redox system cannot overlap with the system under study.
- A quasi (typically Pt) or designed reference is used as a reference electrode.
- System under study is run first then reference redox system is added which cannot affect potential of test redox.



Organic Electrochemistry

Non-aqueous Solvents

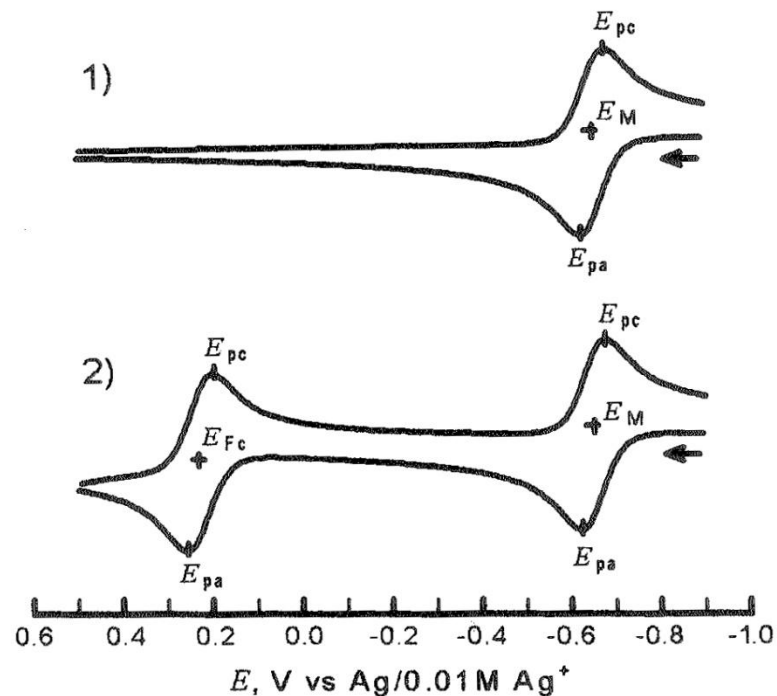
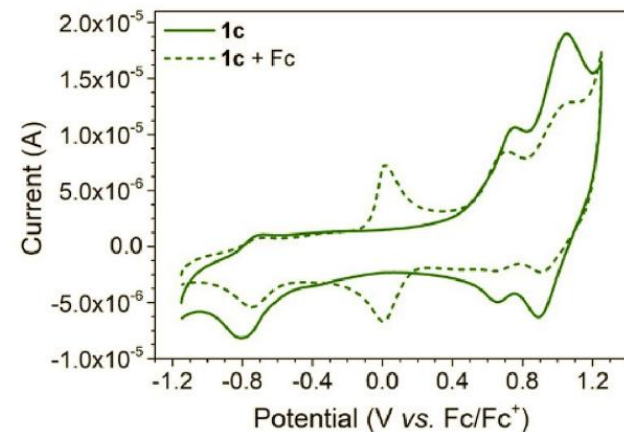
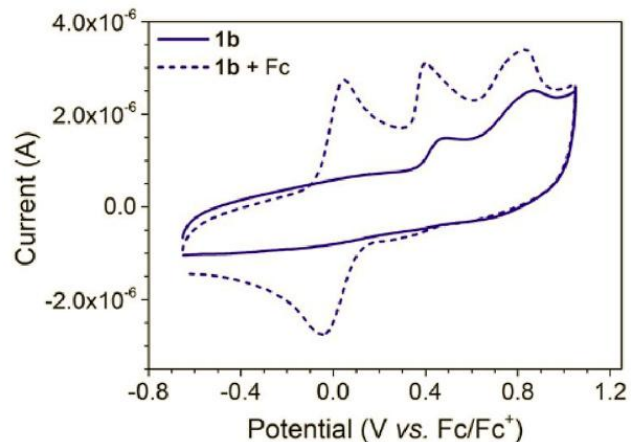
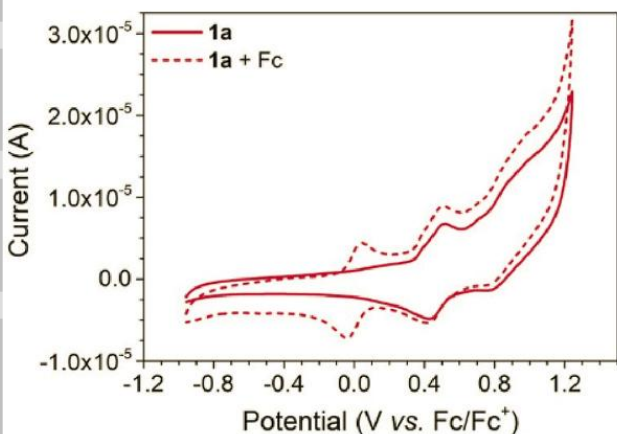


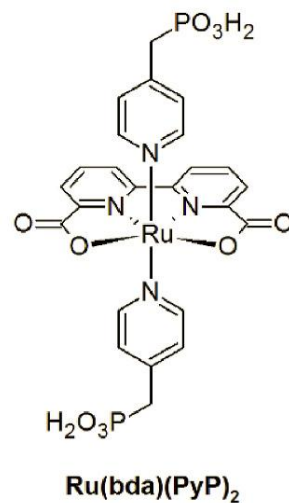
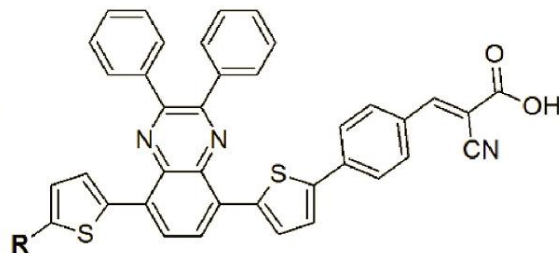
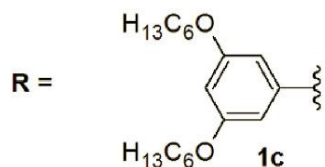
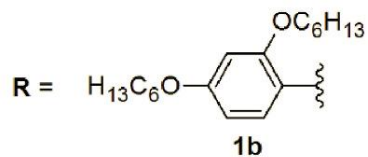
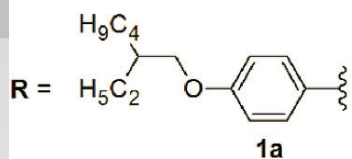
Fig. 6.2 Use of the method recommended by IUPAC for the measurement of electrode potentials: the case of cyclic voltammetry. (a) The system under study (M) only; (b) after addition of the reference system (Fc). If E_M

and E_{Fc} are the half-wave potentials $[=(E_{pc}+E_{pa})/2]$ against the Ag^+/Ag reference electrode, the half-wave potential of M referred to the Fc reference system, $E_{1/2(\text{Fc})}$, is obtained by $E_{1/2(\text{Fc})} = E_M - E_{Fc}$.

Organic Electrochemistry

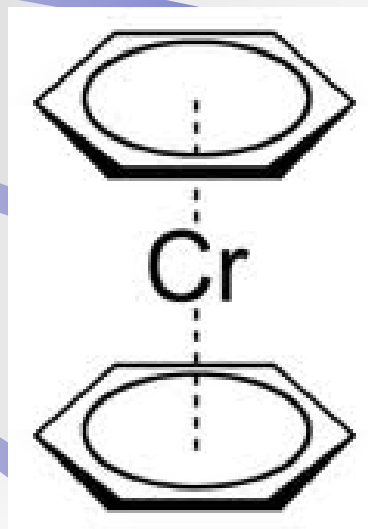
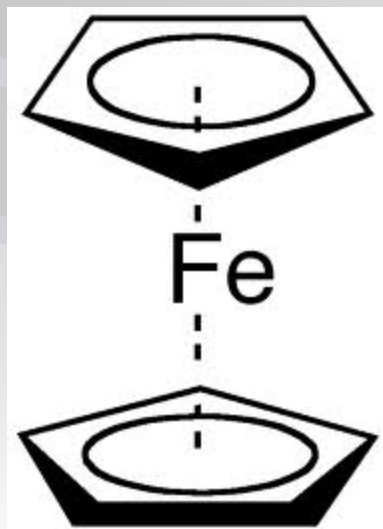


Cyclic voltammetry plots of dyes 1a-c in DCM solution, both without and with ferrocene as an internal standard.



Organic Electrochemistry

The potentials of Fc^+/Fc and BCr^+/BCr couples are almost solvent-independent, making comparison of potentials easy.



Organic Electrochemistry

Non-aqueous Solvents

Tab. 6.4 Potentials of the Ag/Ag⁺ and Hg/Hg²⁺ reference electrodes and Fc/Fc⁺ reference system in various organic solvents (V vs BCr reference redox system; in 0.1 M Bu₄NClO₄ unless otherwise stated in footnote; at 25 °C)

Solvents	E(Ag) ⁴⁾	E(Hg) ⁵⁾	Fc ⁶⁾	Solvents	E(Ag) ⁴⁾	E(Hg) ⁵⁾	Fc ⁶⁾
Alcohols				Nitriles (continued)			
Methanol	1.337		1.134 ¹⁾	Isobutyronitrile	1.071		1.131 ⁷⁾
Ethanol	1.275	1.349	1.134 ¹⁾	Benzonitrile	1.112	1.448	1.149
Ethylene glycol	1.217 ²⁾		1.132 ²⁾	Phenylacetonitrile	1.136	1.469	1.150
Ketones				Nitro compounds			
Acetone	1.315		1.131 ^{1), 7)}	Nitromethane	1.571	1.686	1.112 ¹⁾
Ethers				Nitrobenzene	1.546	1.601	1.140 ⁷⁾
Tetrahydrofuran	1.297	1.367	1.209 ⁷⁾	Aromatic heterocyclic compounds			
Esters, lactones				Pyridine	0.611	0.783	1.149
γ-Butyrolactone	1.364		1.112 ¹⁾	Halogen compounds			
Propylene carbonate	1.514	1.606	1.114 ¹⁾	Dichloromethane	1.562		1.148 ⁷⁾
Amides, lactams, ureas				1,2-Dichloroethane	1.503		1.131
Formamide	1.200		1.135	Sulfur compounds			
N-Methylformamide	1.120 ¹⁾		1.135	Dimethyl sulfoxide	0.958	1.022	1.123 ¹⁾
N,N-Dimethylformamide	1.112	1.144	1.127 ¹⁾	Sulfolane (tetramethylsulfone) ³⁾	1.349		1.114 ¹⁾
N,N-Diethylformamide	1.143		1.142	2,2'-Thiodiethanol	0.691	0.979	1.121
N,N-Dimethylacetamide	1.025		1.135	Tetrahydrothiophene	0.700	0.784	–
N,N-Diethylacetamide	1.027		1.137	N,N-Dimethylthioformamide	0.261	0.501	
N-Methyl-2-pyrrolidinone	1.032	1.118	1.126 ¹⁾	N-Methyl-2-thiopyrrolidone	0.181	0.452	
1,1,3,3-Tetramethylurea	1.036		1.129 ⁸⁾	Hexamethylthiophosphoric triamide	0.445	0.699	1.153
Nitriles				Phosphorus compounds			
Acetonitrile	1.030	1.336	1.119	Trimethylphosphate	1.179	1.292	1.131
Propionitrile	1.026	1.423	1.132	Hexamethylphosphoric triamide	0.891	0.929	1.140
Butyronitrile	1.059	1.427	1.145 ⁸⁾				

1) 0.1 M Et₄NClO₄, 2) 0.05 M Bu₄NClO₄, 3) 30 °C, 4) Ag/0.01 M Ag⁺ (0.1 M Bu₄NClO₄) electrode, 5) Hg/0.01 M Hg²⁺ (0.1 M Bu₄NClO₄) electrode, 6) cyclic voltammetric ($E_{pc} + E_{pa}$)/2 of ferrocene, 7) polarographic $E_{1/2}$, 8) pulse-polarographic E_p . From Gritzner, G. *Pure Appl. Chem.* **1990**, 62, 1839.

Organic Electrochemistry

The cell for organic reactions is a regular three electrode cell.

Working electrode can be Pt, Au, GC, boron-doped diamond with a Pt wire quasi-reference situated close to the WE.

The electroactive species must dissolve in the solvent,

- A polar solvent of weak acidity is suitable for reactions at negative potentials (DMF, DMSO)
- A polar solvent of weak basicity is suitable for reactions at positive potentials (AN)

Organic Electrochemistry

Non-Aqueous Electrolytes

CH₃CN,

DMF,

DMSO,

THF,

Methylene chloride and Ethanol (distillation + storage over 3Å molecular sieves. Storage over activated carbon also)

Organic Electrochemistry

The supporting electrolyte is often

- Tetraalkylammonium salts
- Tetrafluoroborates, hexafluorophosphates, and trifluoromethanesulfonates (R_4NBF_4 , R_4NPF_6 , $R_4NOSO_2CF_3$) are most popular.
 - Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6)
 - Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4)
- $LiClO_4$

Still must be ultrapure.

Organic Electrochemistry

Supporting electrolytes needs to be

- Soluble in the solvent
- Dissociate into ions for conductivity
- Resistant to oxidation and reduction (wide potential window)
- Does not react with analyte
- Available in reasonable purity and cost
- Not toxic or dangerous

Organic Electrochemistry

Tab. 11.1 Examples of supporting electrolytes for use in organic solvents

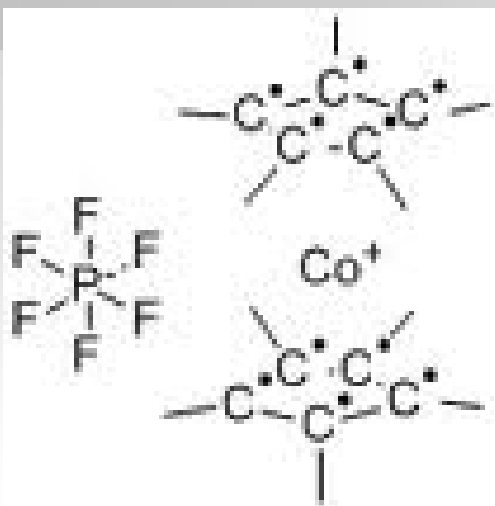
<i>Solvents</i>	<i>Examples of supporting electrolytes¹⁾</i>
HOAc	NaOAc, NH ₄ OAc, LiCl, HCl, H ₂ SO ₄ , HClO ₄ , NaClO ₄ , Bu ₄ NClO ₄ , Bu ₄ NBF ₄
MeOH	NH ₄ Cl, LiCl, HCl, KOH, KOMe, NaClO ₄ , R ₄ N ⁺ salts
en	LiCl, NaNO ₃ , R ₄ N ⁺ salts
DMF	R ₄ N ⁺ , Li ⁺ salts of ClO ₄ ⁻ , BF ₄ ⁻ , PF ₆ ⁻ ; LiCl, NaClO ₄
NMP	R ₄ N ⁺ , Li ⁺ salts of ClO ₄ ⁻ , BF ₄ ⁻ , PF ₆ ⁻ ; LiCl, NaClO ₄
HMPA	R ₄ N ⁺ , Li ⁺ salts of ClO ₄ ⁻ , BF ₄ ⁻ , PF ₆ ⁻ ; LiCl, NaClO ₄
Py	R ₄ N ⁺ salts of ClO ₄ ⁻ , BF ₄ ⁻ ; LiCl, LiClO ₄ , LiNO ₃ , NaI
DMSO	R ₄ N ⁺ , Li ⁺ , Na ⁺ , NH ₄ ⁺ salts of ClO ₄ ⁻ , BF ₄ ⁻ , PF ₆ ⁻ , Cl ⁻ , NO ₃ ⁻
AN	R ₄ N ⁺ , Li ⁺ salts of ClO ₄ ⁻ , BF ₄ ⁻ , PF ₆ ⁻
PC	R ₄ N ⁺ , Li ⁺ salts of ClO ₄ ⁻ , BF ₄ ⁻ , PF ₆ ⁻ ; NaClO ₄
TMS	R ₄ N ⁺ , Li ⁺ salts of ClO ₄ ⁻ , BF ₄ ⁻ , PF ₆ ⁻ ; NaClO ₄ , NH ₄ PF ₆
NM	Bu ₄ N ⁺ , Li ⁺ salts of ClO ₄ ⁻ , BF ₄ ⁻ , PF ₆ ⁻
NB	Bu ₄ NClO ₄
THF, DME	Bu ₄ NClO ₄ , NaClO ₄ , LiClO ₄
CH ₂ Cl ₂	Bu ₄ N ⁺ , Hex ₄ N ⁺ salts of ClO ₄ ⁻ , BF ₄ ⁻ , PF ₆ ⁻
Benzene	Bu ₄ NBF ₄ , Hex ₄ NClO ₄

1) When a mercury electrode is used, alkali metal salts are not appropriate because the potential window is narrow on the negative side.

Organic Electrochemistry

Organometallic complexes are best studied in organic solutions since most are insoluble in aqueous solutions.

Example: cobalticinium



Organic Electrochemistry

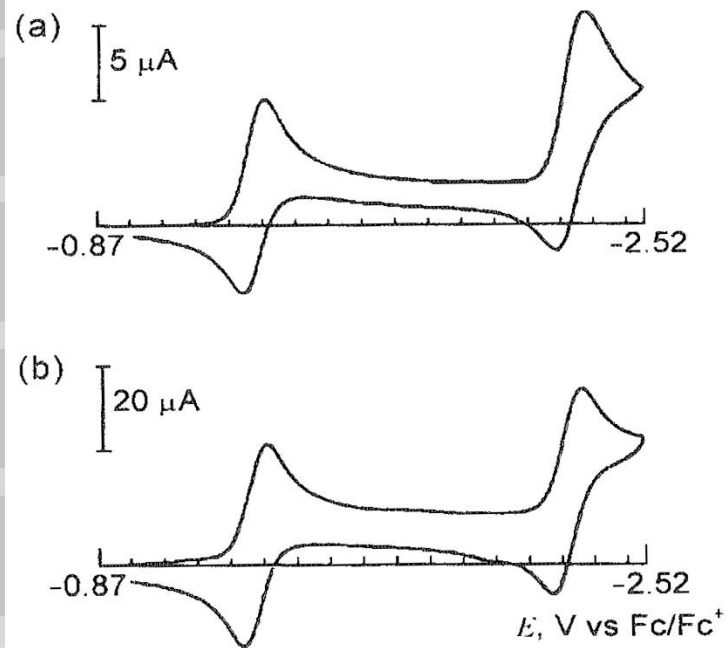


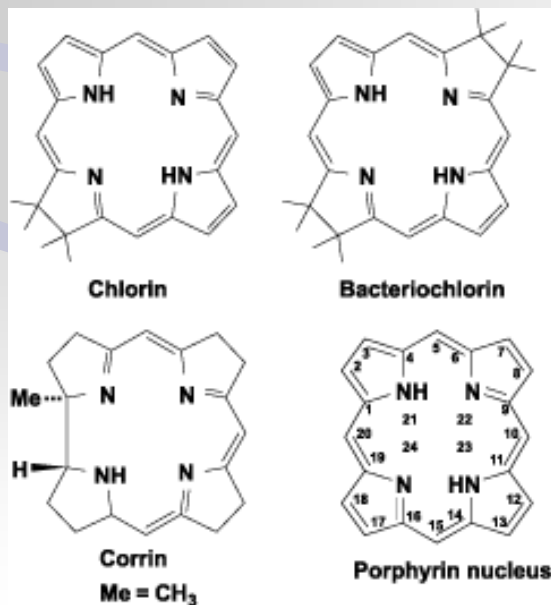
Fig. 8.7 Cyclic voltammograms of cobalticinium ion in 1 mM $(\eta\text{-C}_5\text{H}_5)_2\text{CoPF}_6$ -0.1 M $\text{Bu}_4\text{NBF}_4\text{-AN}$ [30a]. Recorded using a hanging mercury drop electrode (a) and a glassy carbon electrode (b) at 100 mV s^{-1} and at 25 °C.

- 5) The dynamical solvent effects on the kinetics of electron-transfer processes have been reviewed in detail in Refs [24a] and [32] and concisely in Section 3.6 of Ref. [8].

Organic Electrochemistry

Porphyrins and Metalloporphyrins

Class of cyclic compounds in which the parent macrocycle consists of four pyrrole-type units linked together by single carbon bridges which carry out vital biochemical processes in living organisms.



Organic Electrochemistry

Metalloporphyrins can have up to three electroactive sites:

- Metal-free porphyrin can form radical anion and dianion and can form radical cation and dication
- Metal center can be oxidized and reduced
- Axial ligands can be electroactive

Organic Electrochemistry

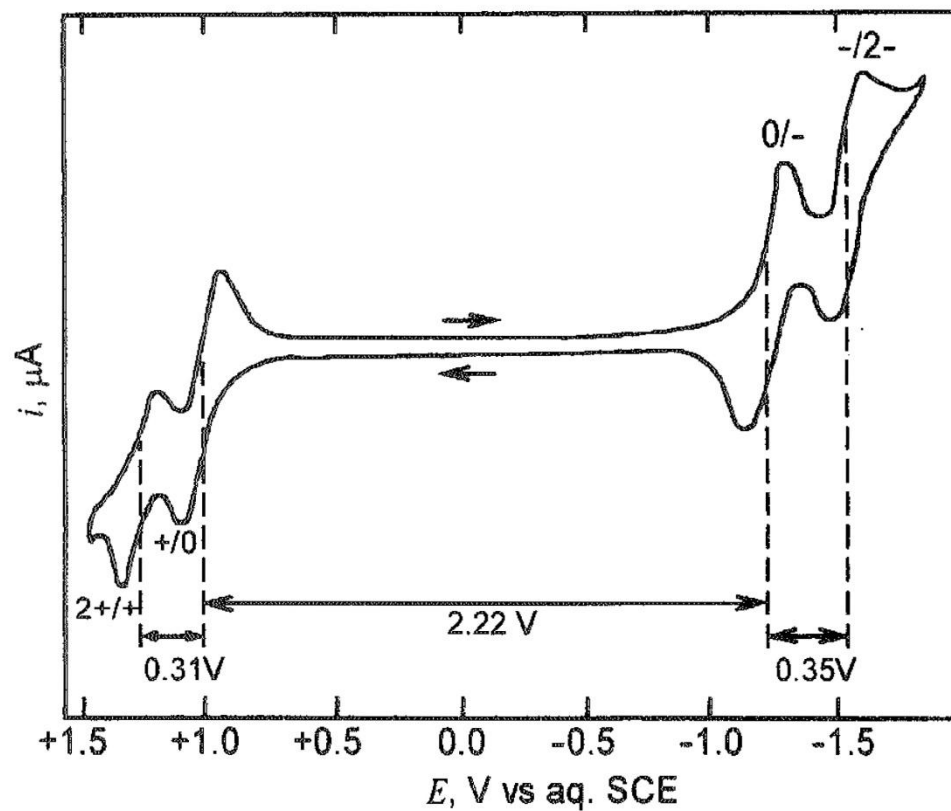
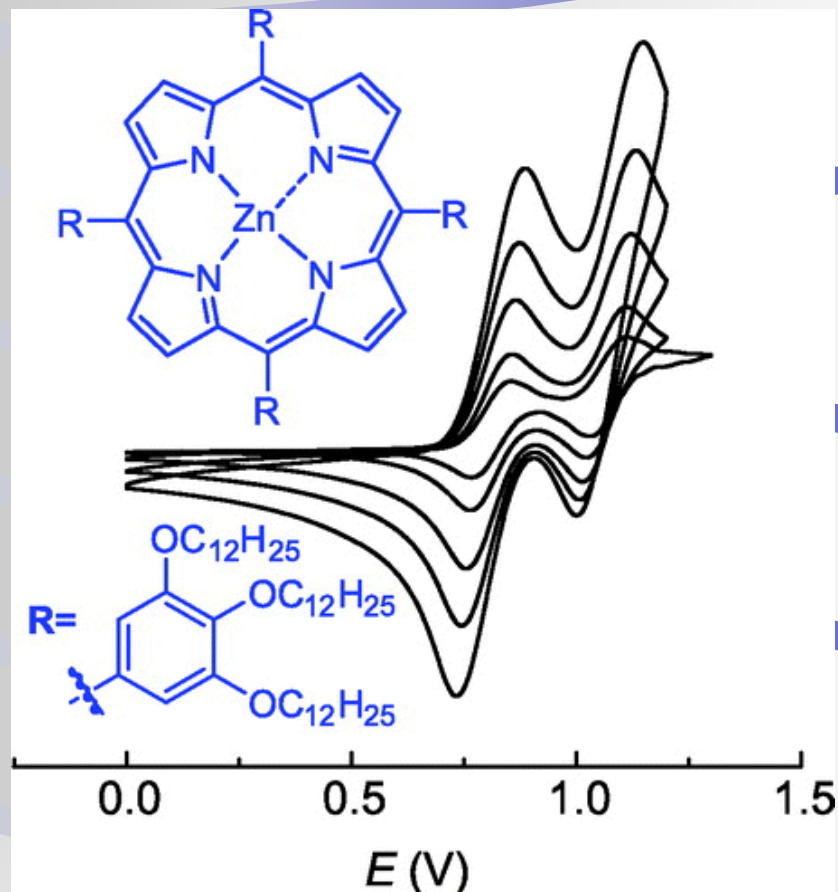


Fig. 8.9 Cyclic voltammogram of tetraphenylporphyrin (TPPH_2) at a platinum electrode in a solution of 2.6 mM TPPH_2 -0.1 M Bu_4NClO_4 - CH_2Cl_2 [32 a].

Organic Electrochemistry



CV established that each porphyrin underwent two reversible one-electron oxidations at 492 and 725 mV (vs Fc/Fc⁺ (ferrocene reference)) for the free-base porphyrin and at 329 and 589 mV (vs Fc/Fc⁺) for the Zn-metalloporphyrin.

Electron-transfer rates were also determined to fall between 1.2×10^{-3} and 2.4×10^{-3} cm s⁻¹.

Organic Electrochemistry

Reduction of organic compounds

- Outer sphere type
- Dissociation type

Outer sphere reductions usually are a one-electron process producing a radical anion,

$Q^{\cdot-}$



Organic Electrochemistry

$Q^{\cdot-}$, is generally reactive, but its lifetime varies depending on the environment.

Aprotic solvents, i.e. tetraalkylammonium salts, help stabilize the radical, and can be studied using CV.

Organic Electrochemistry

Tab. 8.6 Standard rate constants for electrode reductions of organic compounds determined by an AC impedance method

Compound	$E'_{1/2}$ V vs SCE	$k_{s,exp}$ $cm\ s^{-1}$	α	$(\phi_{OHP}-\phi_s)$, mV	$k_{s,corr}$ $cm\ s^{-1}$	k_{ex} $M^{-1}\ s^{-1}$
Benzonitrile	-2.17	0.61	0.64	-83	4.9	5.5×10^8
Nitrobenzene	-1.05	2.2	0.70	-56	10	3.0×10^7
<i>m</i> -Dinitrobenzene	-0.76	2.7	0.50	-46	6.5	5.2×10^8
<i>p</i> -Dinitrobenzene	-0.55	0.93	0.61	-36	2.2	6.0×10^8
Dibenzofuran	-2.41	2.9	(0.57)	-89	21	1.6×10^9
Dibenzothiophene	-2.37	1.6	(0.57)	-88	12	1.2×10^9
1,4-Naphthoquinone	-0.52	2.1	(0.57)	-35	4.6	4.2×10^8
Anthracene	-1.82	5	0.55	-76	27	1.8×10^9
Perylene	-1.54	5	0.50	-70	20	2.1×10^9
Naphthalene	-2.49	1.0	0.56	-145	23	6.2×10^8
<i>trans</i> -Stilbene	-2.15	1.2	0.58	-139	27	1.0×10^9

$E'_{1/2}$ reversible half-wave potential, $k_{s,exp}$ experimental standard rate constant, α transfer coefficient, $(\phi_{OHP}-\phi_s)$ potential at the outer-Helmholtz plane, $k_{s,corr}$ standard rate constant after correction for the double-layer effect (see ⁴⁾), k_{ex} rate constant for the homogeneous self-exchange electron-transfer (see ⁴⁾ in Chapter 9); obtained with a HMDE in DMF-0.5 M Bu_4NClO_4 at $22 \pm 2^\circ C$, except the last two obtained with a DME in DMF-0.1 M Bu_4NI at $30^\circ C$.

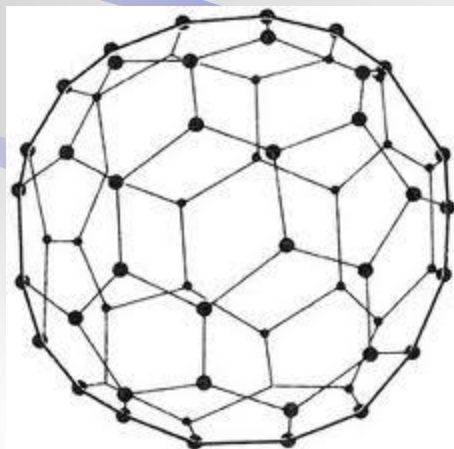
From Kojima, H., Bard, A.J. *J. Am. Chem. Soc.* 1975, 97, 6317.

Organic Electrochemistry

Outer sphere type

Example: Buckminsterfullerene (C_{60}) in AN/toluene at $-10\text{ }^{\circ}\text{C}$

Has six one-electron reversible steps in CV, can accept up to six electrons to form diamagnetic, C_{60}^{6-} , because its LUMO is triply degenerate.



Organic Electrochemistry

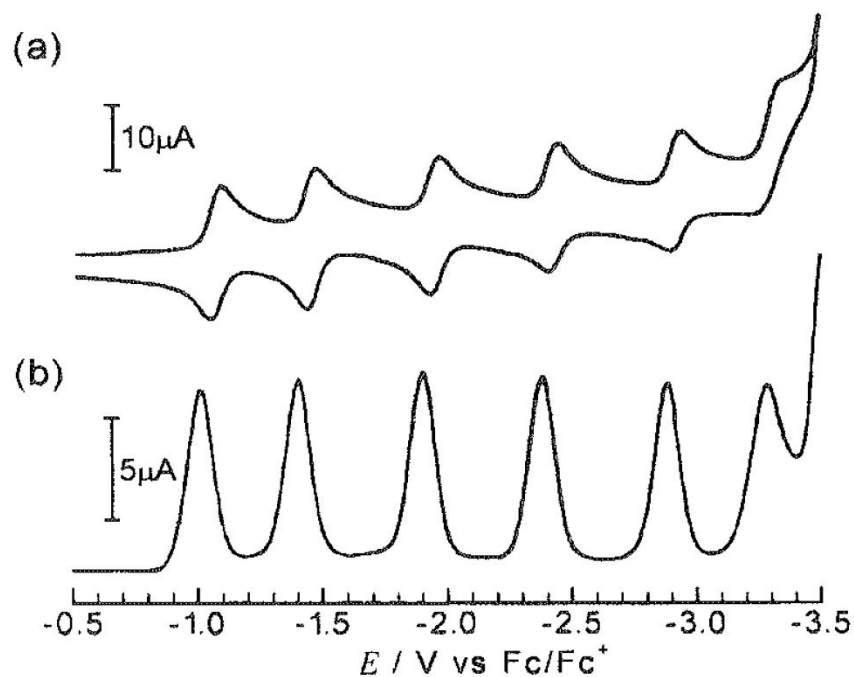


Fig. 8.13 Reduction of fullerene, C_{60} , in AN-toluene (1:5) with Bu_4NPF_6 as supporting electrolyte at -10°C , recorded using (a) cyclic voltammetry at 100 mV s^{-1} and (b) differential pulse voltammetry at 25 mV s^{-1} . $E_{1/2}$: -0.98 , -1.37 , -1.87 , -2.35 , -2.85 and $-3.26\text{ V vs Fc/Fc}^+$ [52].

Organic Electrochemistry

Can see from the example before that the potentials for aromatics depend on the HOMO/LUMO splitting.

$$-nFE_{ox}^{\circ} = HOMO + C_{solvation} + D_{reference\ electrode}$$

For example, when the electrons in the electrode are at a higher energy than the LUMO of a molecule, an electron from the electrode is transferred to the molecule.

Organic Electrochemistry

HOMO

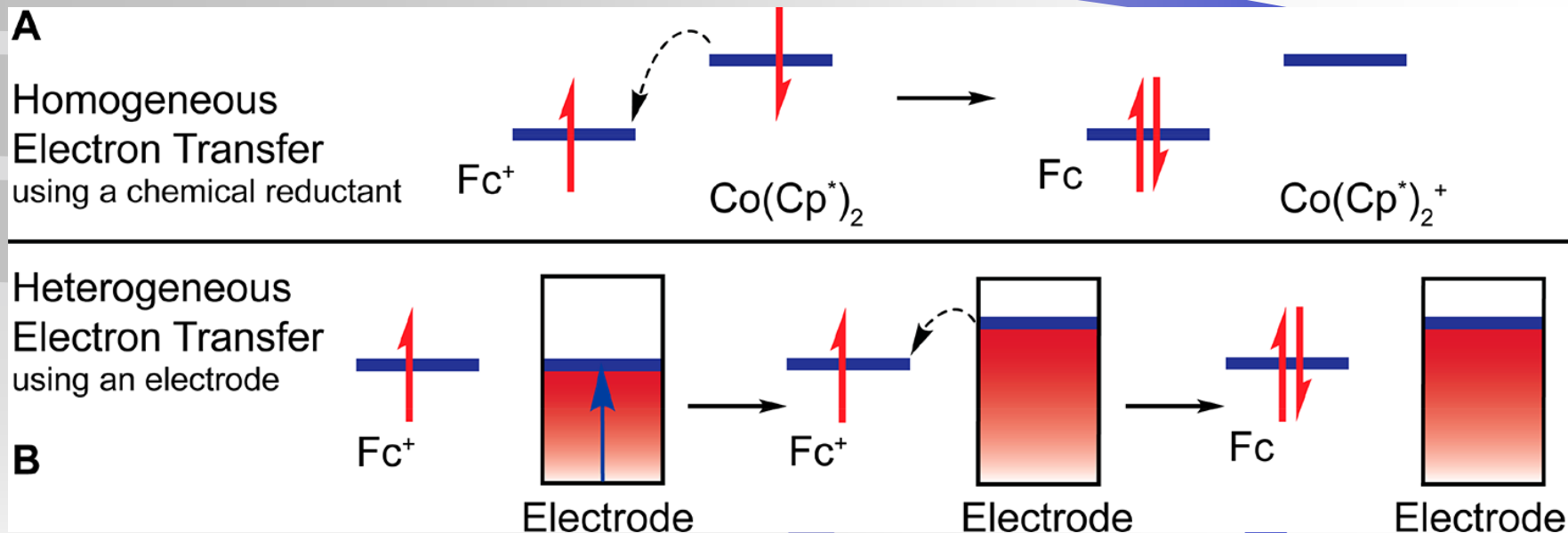
- The HOMO is the highest energy orbital that is fully occupied by electrons in a molecule.
- It represents the highest energy molecular orbital from which an electron can be excited to a higher energy level, such as the LUMO.
- The energy of the HOMO is critical in determining the molecule's ability to donate electrons (i.e., its oxidation potential).

LUMO

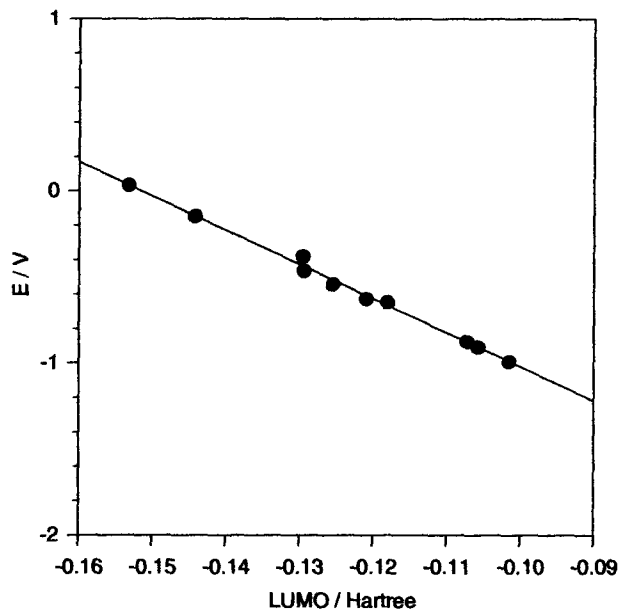
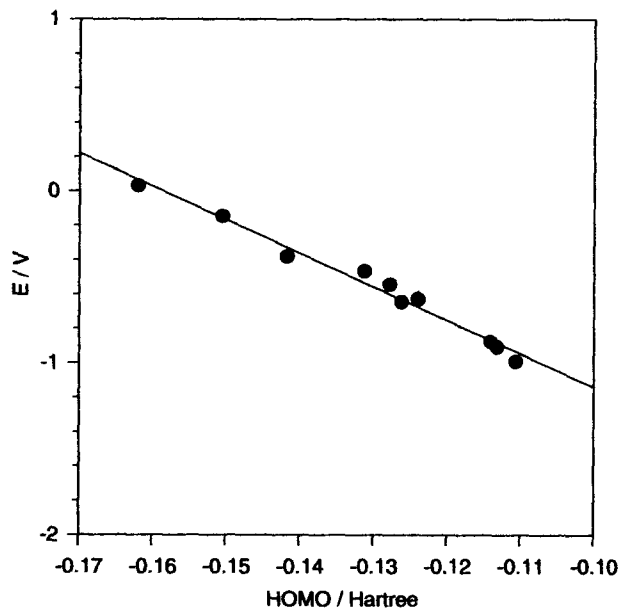
- The LUMO is the lowest energy orbital that is not occupied by electrons.
- It represents the frontier molecular orbital that can accept an electron from the HOMO or another electron donor.
- The energy of the LUMO is important in determining the molecule's ability to accept electrons (i.e., its reduction potential).

Organic Electrochemistry

For example, when the electrons in the electrode are at a higher energy than the LUMO of a molecule, an electron from the electrode is transferred to the molecule.



Organic Electrochemistry



Prediction of one-electron electrode potentials of some quinones in dimethylsulfoxide, *J. Electroanal. Chem.*, **2004**, 573, 49-53; M. Namazian, P. Norouzi

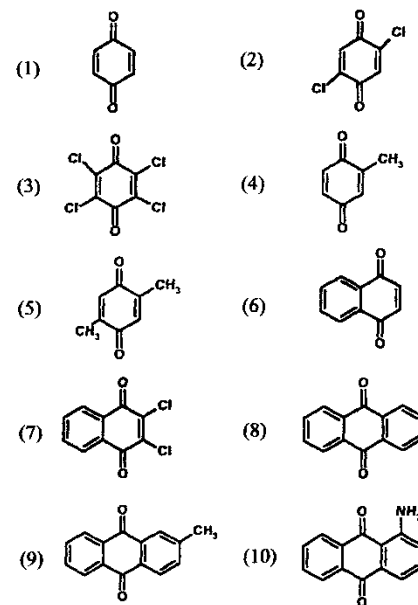
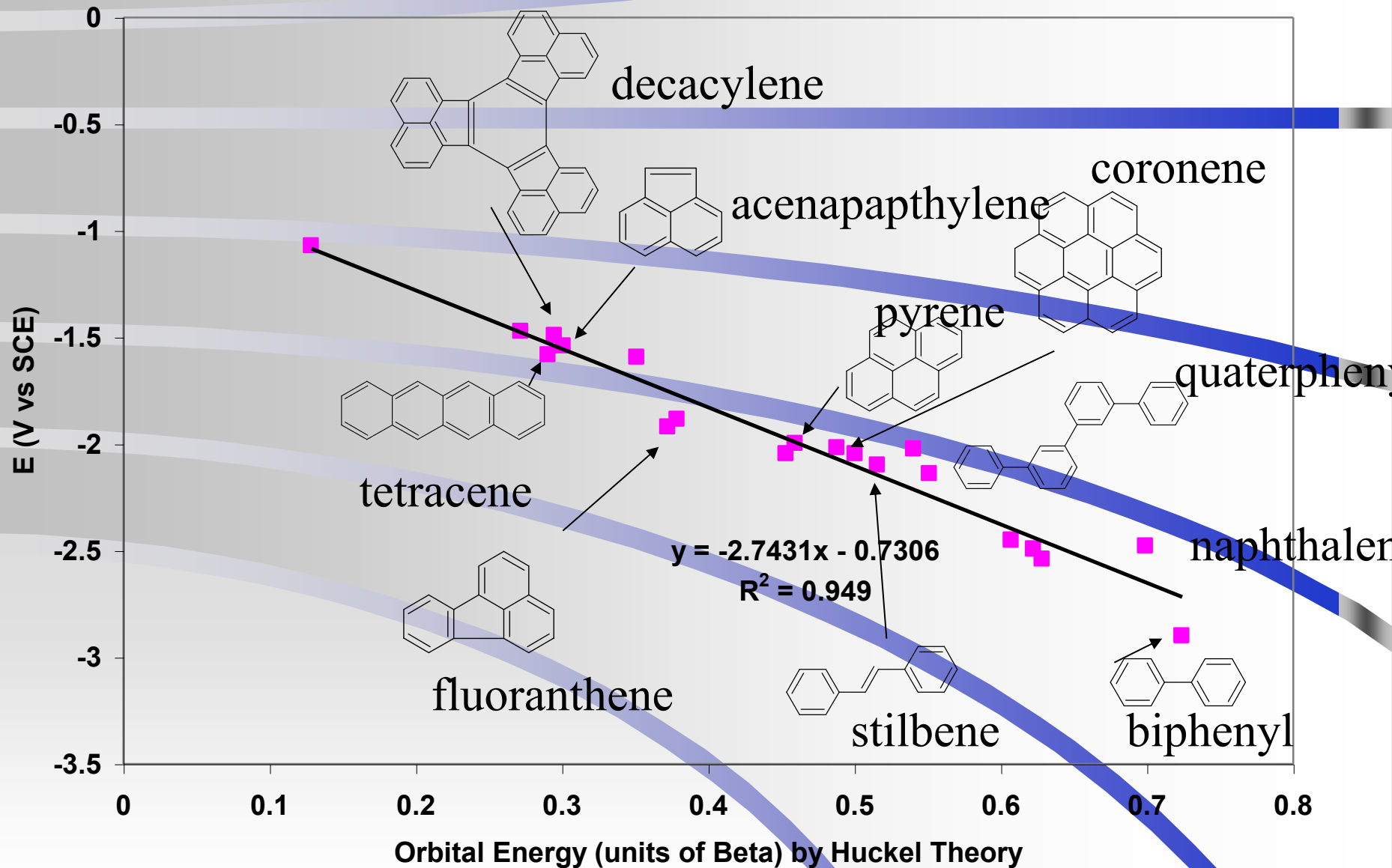
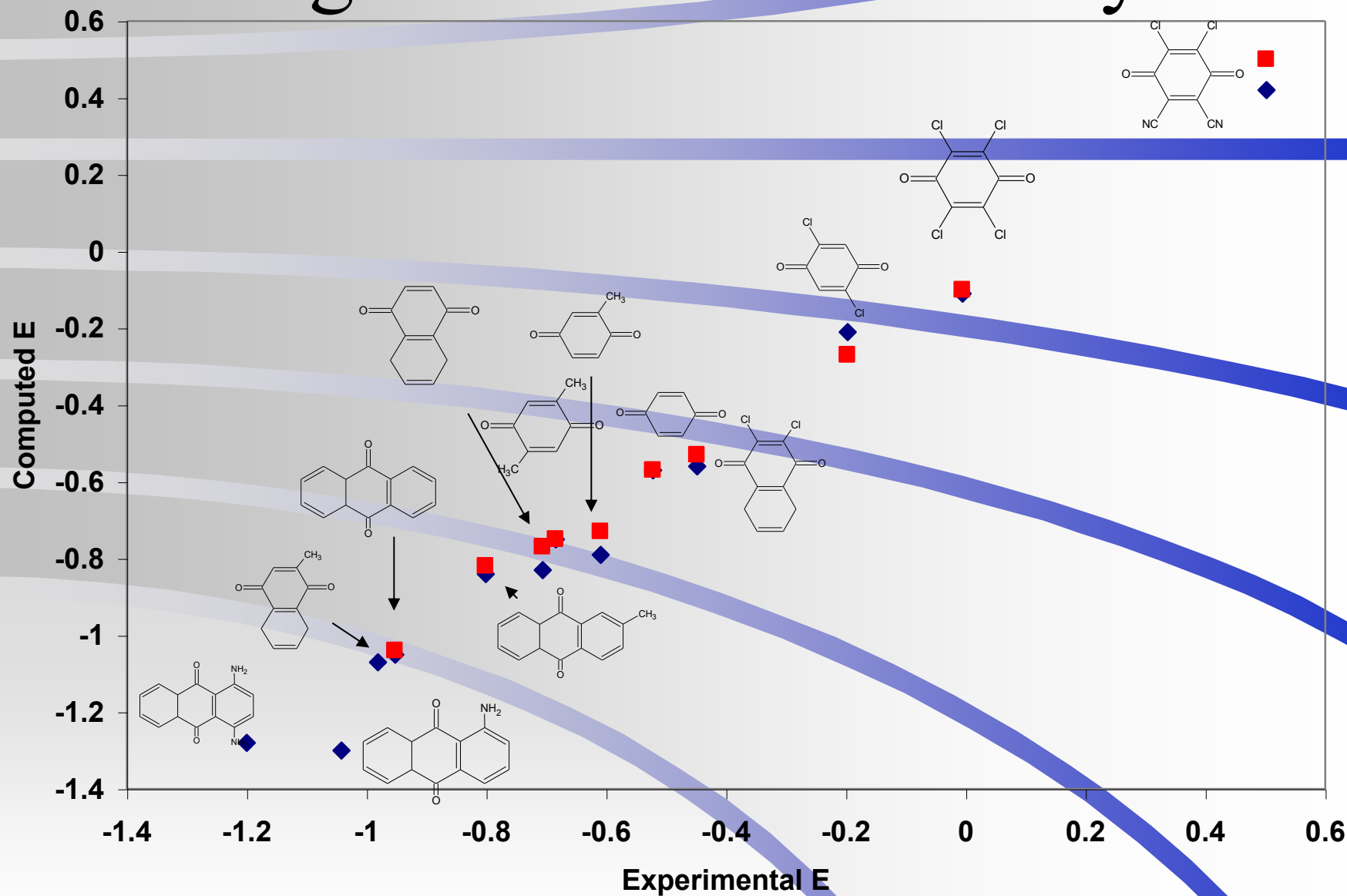


Fig. 2. Oxidised forms of the molecules studied.

Organic Electrochemistry



Organic Electrochemistry



Accurate Calculation of Absolute One-Electron Redox Potentials of Some para-Quinone Derivatives in Acetonitrile, *JPCA*, **2007**, 111, 7227, Namzian and Coote.

CHEM 5390

Organic Electrochemistry

With organic solvents can run CV at low temperatures.

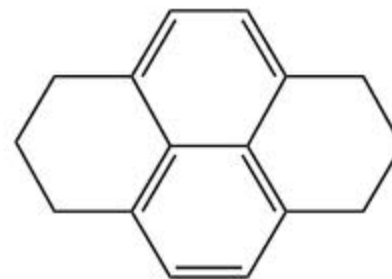
This makes it convenient to study electrode reactions involving unstable products or intermediates.

Lowering temperature by 30-40 °C decreases the reaction rate of the unstable species to one-tenth of original value.

Organic Electrochemistry

Example

1, 2, 3, 6, 7, 8-hexahydropyrene



At room temperature, there is no reduction peak (appears irreversible). However at $-60\text{ }^{\circ}\text{C}$, both oxidation and reduction waves appear in the CV.

Organic Electrochemistry

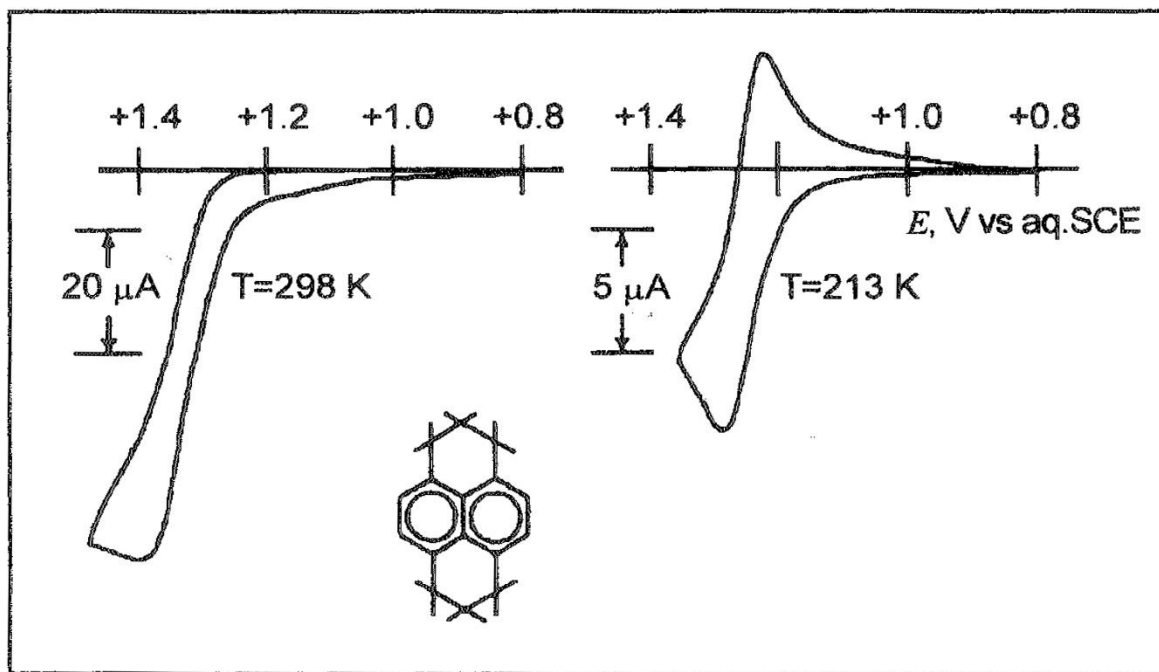


Fig. 8.22 Effect of temperature on the cyclic voltammogram for the oxidation of 1,2,3,6,7,8-hexahydropyrene (2.5 mM) at a platinum electrode in 0.1 M $\text{Bu}_4\text{NClO}_4^-$ butyronitrile. Scan rate: 50 mV s^{-1} [76 a]

Organic Electrochemistry

Tab. 8.10 Solvent-supporting electrolyte couples for low-temperature electrochemistry¹⁾

<i>Solvent</i> ²⁾	<i>F_p</i> (°C)	<i>Supporting electrolyte</i>	<i>Lowest temp.</i> (°C)
Ac	-94.7	0.3 M Et ₄ NPF ₆	-75
AN	-43.8	0.1 M Bu ₄ NClO ₄	-45
BuN	-111.9	0.3 M Bu ₄ NClO ₄	-75
CH ₂ Cl ₂	-94.9	0.5 M Bu ₄ NClO ₄ ; 0.1 M Bu ₄ NPF ₆	-90
DMF	-60.4	0.6 M Bu ₄ NClO ₄ ; 0.6 M Bu ₄ NPF ₆	-60
EtOH	-114.5	0.5 M LiClO ₄	-103
PrN	-92.8	0.1 M Bu ₄ NClO ₄	-100
THF	-108.4	0.2 M Bu ₄ NClO ₄	-78
BuN/C ₂ H ₅ Cl (1:1 by volume)		0.2 M Bu ₄ NClO ₄	-185
DMF/toluene (2:3 by volume)		0.1 M Et ₄ NPF ₆	-88
C ₂ H ₅ Cl/THF/2-MeTHF (2:0.88:0.12 by volume)		0.6 M LiBF ₄	-173

1) Prepared from the data in Table 16.2 of Ref. [77].

2) For abbreviated symbols, see Table 1.1.

Organic Electrochemistry

Study of organic molecules (biological)

Oxidation of Adrenaline

An ECE reaction which can be studied with CV. The reaction is pH dependent.

Organic Electrochemistry

Oxidation of Adrenaline

It is a reversible reaction at pH close to 0.

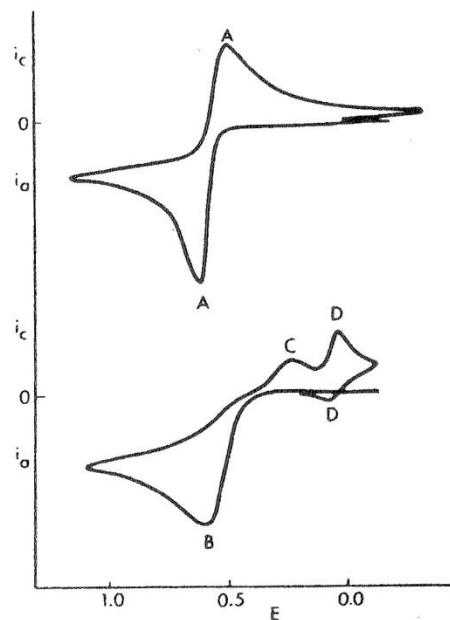
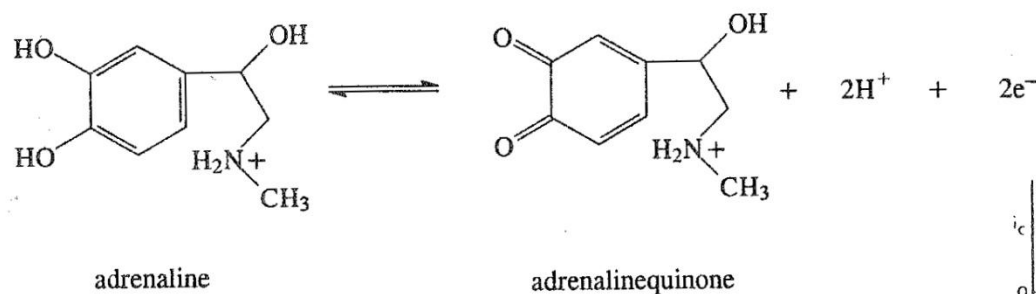
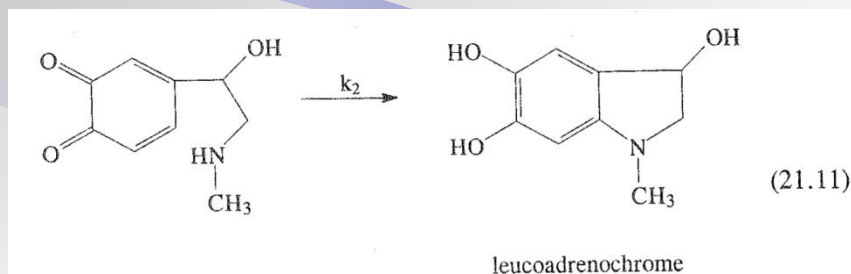
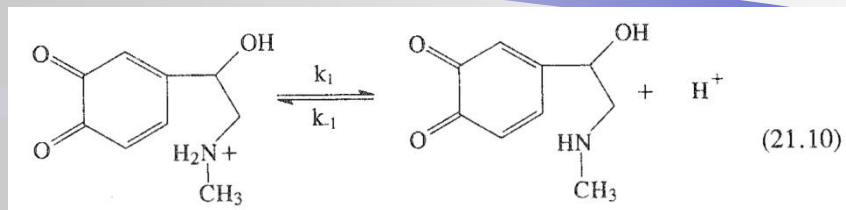


Figure 21.4 (Top) Cyclic voltammogram of adrenaline in 0.29 M HClO₄ at a scan rate of 55 mV/s. (Bottom) Cyclic voltammogram of adrenaline at pH 3.0 at a scan rate of 278 mV/s. [From Ref. 2, reprinted with permission.]

Organic Electrochemistry

Oxidation of Adrenaline

However – raise the pH and the deprotonation of the conjugate acid occurs leading to cyclization.



Organic Electrochemistry

Oxidation of Adrenaline

However – raise the pH and the deprotonation of the conjugate acid occurs leading to cyclization.

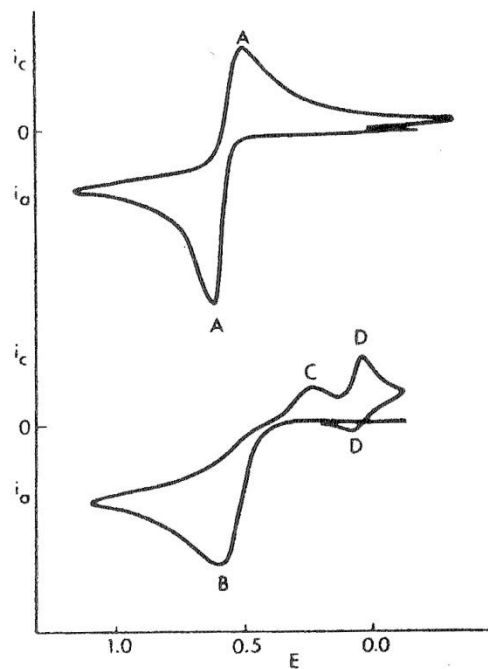
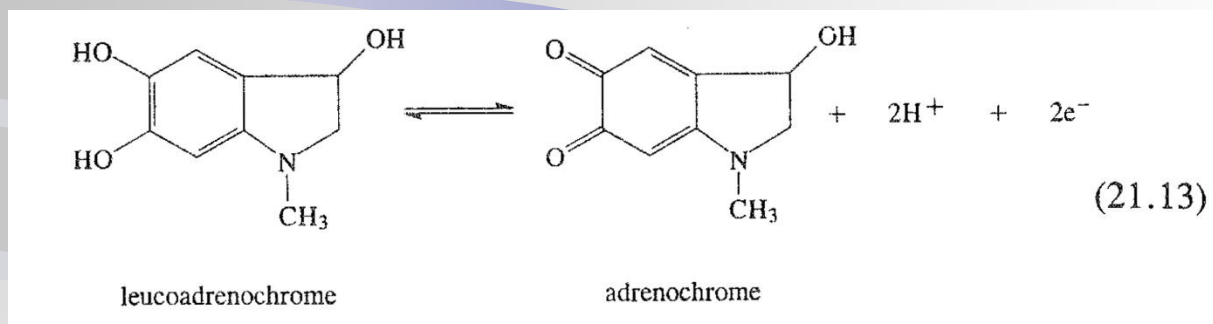


Figure 21.4 (Top) Cyclic voltammogram of adrenaline in 0.29 M HClO₄ at a scan rate of 55 mV/s. (Bottom) Cyclic voltammogram of adrenaline at pH 3.0 at a scan rate of 278 mV/s. [From Ref. 2, reprinted with permission.]

Organic Electrochemistry

Oxidation of Adrenaline

However – raise the pH and the deprotonation of the conjugate acid occurs leading to cyclization. The cyclic compound formed is electrochemically active (reversible) (D).



Organic Electrochemistry

Heeger, MacDiarmis, and Shirakawa discovered that doping polyacetylene (PA) with iodine gave the polymer metallic properties, increasing conductivity. (1977) (Noble prize 2000)

This introduced the field of conducting polymers.

Organic Electrochemistry

Conducting polymers include:

- Polyphenylene (PP)
- Polypyrrole (PPy)
- Polyaniline (PAN)
- Polythiophene (PTh)
- Polyphenylvinyls (PV)

Organic Electrochemistry

Anodic oxidation of a suitable monomer (i.e. pyrrole, thiophene, aniline) is used to prepare these polymers.

These polymers are now used in battery electrodes, electrochromic displays, sensors, anticorrosives, electrocatalysts, antistatic materials, light-emitting materials (OLED).

Organic Electrochemistry

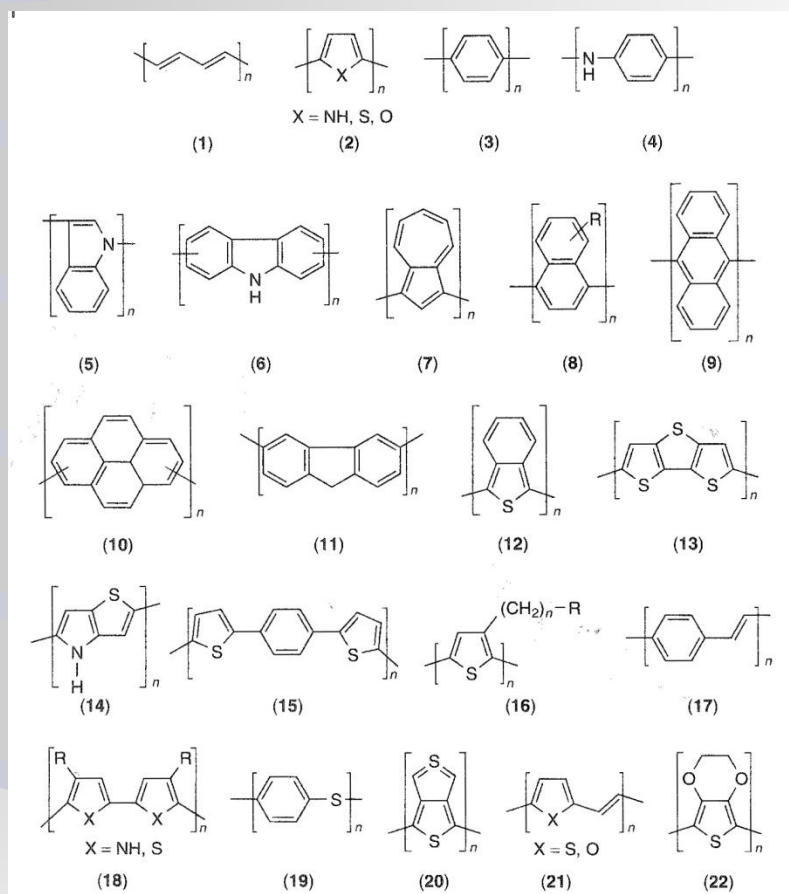


Fig. 1 Building units of conducting polymers, (1): polyacetylene (PA); (2): polypyrrole (PPy), polythiophene (PTh), polyfuran (PFu); (3): polyphenylene (PP); (4): polyaniline (PANI); 5: polyindole (PIND); (6): polycarbazole (PCaz); (7): polyazulene (Paz); (8): polynaphthalene (PNa); (9): polyanthracene (PAnth); (10): polypyrene (PPyr); (11): polyfluorene (PFlu); (12): poly(isothionaphthalene) (PITN); (13): poly(dithienothiophene); (14): poly(thienopyrrole); (15): poly(dithienylbenzene); (16): poly(3-alkylthiophene); (17): poly(phenylene vinylene); (18): poly(bipyrrole) (PBPy), poly(bithiophene) (PBT); (19): poly(phenylenesulfide); (20): 4-poly(thienothiophene); (21): poly(thienyl vinylene), poly(furane vinylene); (22): poly(ethylenedioxythiophene) (PEDOT).

Organic Electrochemistry

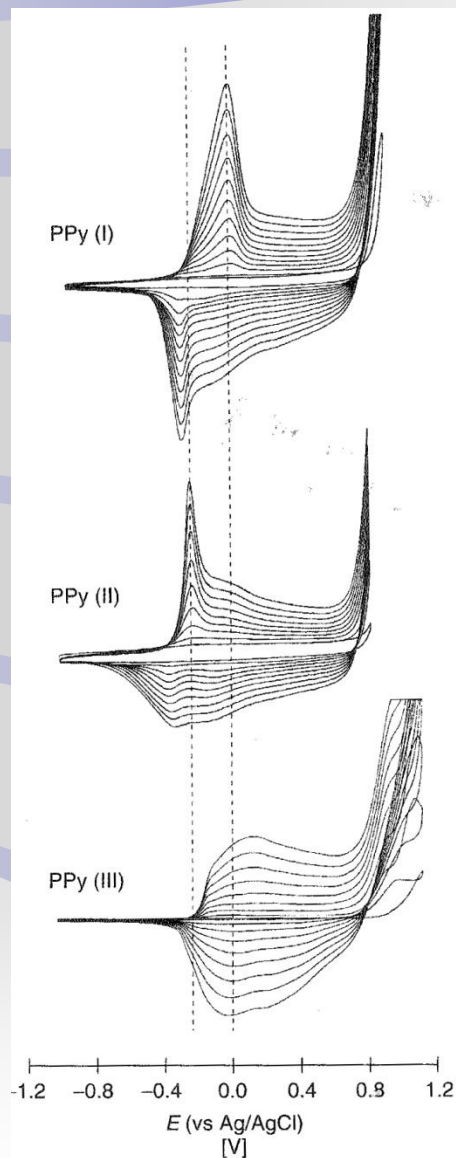


Fig. 7 PPy variants generated by galvanostatic or potentiodynamic techniques. PPy (I) is formed in acetonitrile with 1% water. The average conjugation length is about 30 units. The material is weakly cross-linked. PPy (II) is formed at low oxidation potentials (≤ 0.75 V versus Ag/AgCl) or low current densities ($6 \mu\text{A cm}^{-2}$). It consists of short chains with σ -dimers in the charged state. PPy (III) showing symmetric voltammograms during charging and discharging cycles is a strongly cross-linked material. [From Ref. [73].]

Organic Electrochemistry

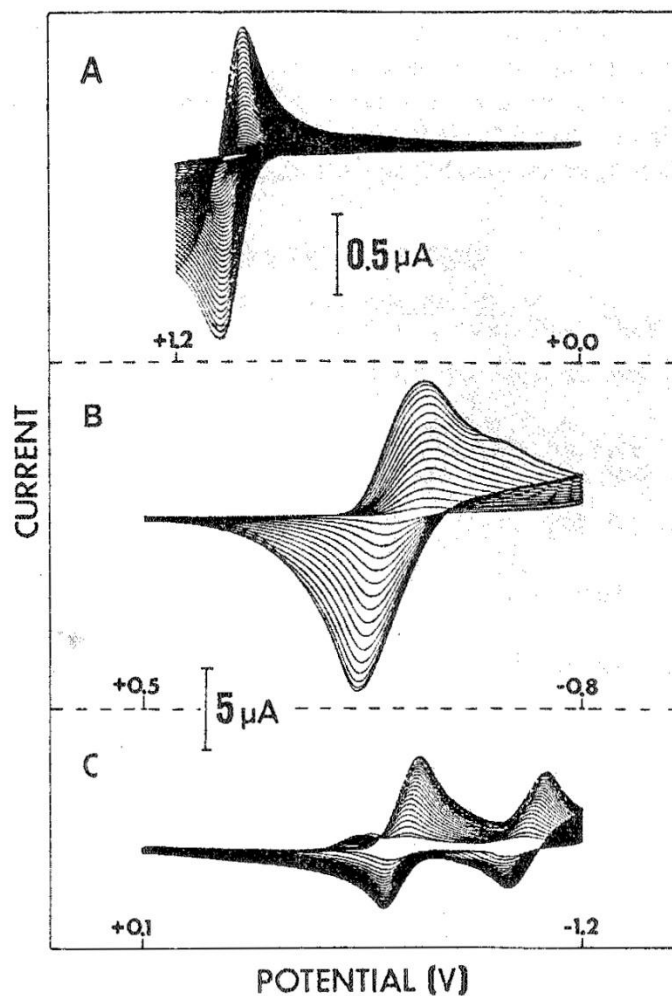


Figure 3. Cyclic voltammograms for 1×10^{-4} M $\text{Ru}(\text{bpy})_3^{2+}$ (A), $\text{Ru}(\text{NH}_3)_6^{3+}$ (B), and MV^{2+} (C) recorded continuously at a glassy carbon electrode coated with Eastman-AQ film. Scan rate is 20 mV/s; other conditions are as in Figure 1.

Class Assignment

- Read Chapters 1, 2, 4, 5, 6, 7, 12, 13, and 15
“Electrochemical Methods” Bard
- Exam 1 – Oct 16th

