

INTRODUCTION: BASIC CONCEPTS AND A BRIEF HISTORY OF ORGANIC REDOX SYSTEMS

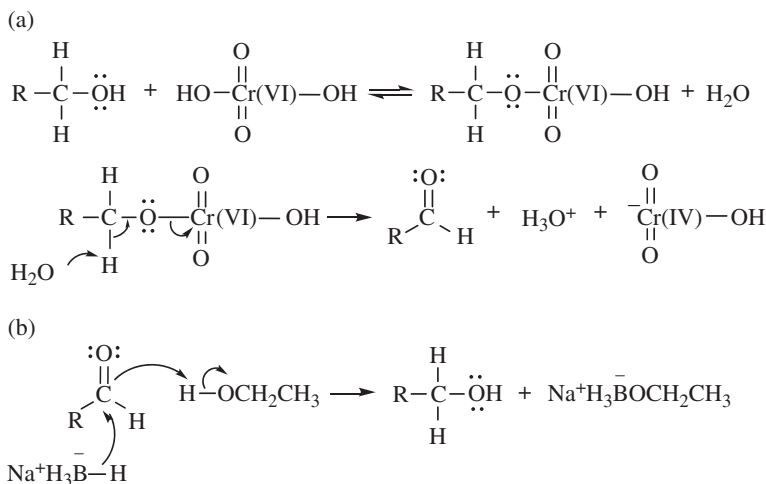
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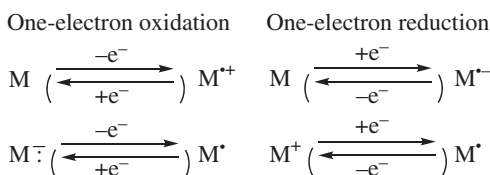
1.1 REDOX REACTION OF ORGANIC MOLECULES

Redox is a portmanteau word of “reduction” and “oxidation.” Originally, oxidation meant a chemical reaction in which oxygen combines with another substance, after Antoine Lavoisier, late in the eighteenth century, called a product of the reaction an oxide [1]. The term “reduction” had been used long before the introduction of the term “oxidation” in the smelting to produce iron from ore and coke [1]. In the contemporary definition recommended by IUPAC [2], oxidation is a reaction that satisfies criteria 1 “the complete, net removal of one or more electrons from a molecular entity” and 2 “an increase in the oxidation number of any atom within any substrate” and meets in many cases criterion 3 “gain of oxygen and/or loss of hydrogen of an organic substrate.” Conversely, reduction is the reverse process of oxidation.

For transition metals, a direct one-electron transfer related to the aforementioned criterion 1 is common due to their relatively lower ionization energy in comparison with main group elements [3] and low reactivity of the unpaired d-electrons. In contrast, the mechanisms of common organic redox reactions do not involve a direct one-electron transfer [4], and reactions based on the criterion 3 are typical. For example, oxidation of primary alcohol (RCH_2OH) to aldehyde (RHC=O) with Cr(VI)O_3 proceeds via chromic ester intermediate ($\text{RCH}_2\text{O}_3\text{Cr(VI)OH}$), and proton



SCHEME 1.1 (a) Oxidation of alcohol to aldehyde with Cr(VI) and (b) hydride reduction of aldehyde to alcohol.



SCHEME 1.2 One-electron oxidation and reduction of neutral and ionic molecules.

and $\text{HOCr}(\text{IV})\text{O}_2^-$ are eliminated from the intermediate [5] (Scheme 1.1a). In this reaction, the total number of electrons in the outer shell decreases from 14 at the C–O moiety to 12 at the C=O moiety, that is, two-electron oxidation, while the formal oxidation number of Cr changes from +6 to +4, that is, two-electron reduction. Similarly, reduction of carbonyl group to alcohol with NaBH_4 in ethanol formally proceeds via nucleophilic attack of a pair of electrons in hydride to electron-deficient carbonyl carbon [5] (Scheme 1.1b). Thus, formally, a pair of two electrons moves together in typical organic redox reactions as known in other organic reactions such as substitutions.

On the other hand, one-electron oxidation or reduction of a neutral or ionic molecule (Scheme 1.2) gives generally highly reactive ion radicals or radicals, and follow-up reactions such as radical coupling and deprotonation are prone to take place [6]. Nevertheless, some organic molecules give persistent species after one-electron transfer at ambient temperature [7, 8]. Simple π -extension and substituents of resonance electron donating $\text{R}_2\text{N}-$, $\text{RO}-$, $\text{RS}-$ or withdrawing $\text{N}\equiv\text{C}-$, $\text{C}=\text{O}$ groups cause delocalization of spin and charge density, which reduces the reactivity of the reactive center. As the other thermodynamic stabilization, aromatization after electron transfer plays an important role for certain molecules. An appropriate steric protection is also an effective strategy for protecting a reactive radical center [9]. As a result of

these effects, they can be reversibly regenerated by the reverse electron transfer. This book deals with organic π -electron systems and related organo main group compounds that show such reversible one-electron transfer.

1.2 REDOX POTENTIAL IN NONAQUEOUS SOLVENTS

Redox potential is the important measure for redox systems, by which one can predict how easily one-electron oxidation or reduction takes place with other redox reagents. For the measurement of redox potential, cyclic voltammetry is usually the first choice, because not only the redox potential but also the stability of the species generated after electron transfer can be observed. Several types of reference electrodes are used to measure redox potentials. The standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE), which is determined by redox potential of $2\text{H}^+/\text{H}_2$ couple in an aqueous media, is defined as 0V in standard electrode potential. However, since the setting of apparatus of SHE is complicated, other reference electrode such as saturated calomel electrode (SCE) and saturated Ag/AgCl or Ag/Ag⁺ electrode is commonly used for routine laboratory experiments. A saturated aqueous KCl solution is used for SCE and saturated Ag/AgCl electrodes, while polar solvent, for example, acetonitrile can be used for Ag/Ag⁺ electrode.

As for the absolute electrode potential, the value -4.44 ± 0.02 V vs NHE (25°C in H₂O) is recommended by IUPAC [10]. The standard and absolute electrode potentials of NHE, SCE (=0.244 V vs NHE 25°C in H₂O) [11], and saturated Ag/AgCl (=0.199 V vs NHE 25°C in H₂O) [12] are shown in Figure 1.1. Since the potential of Ag/Ag⁺ electrode in a nonaqueous solvent varies with the conditions

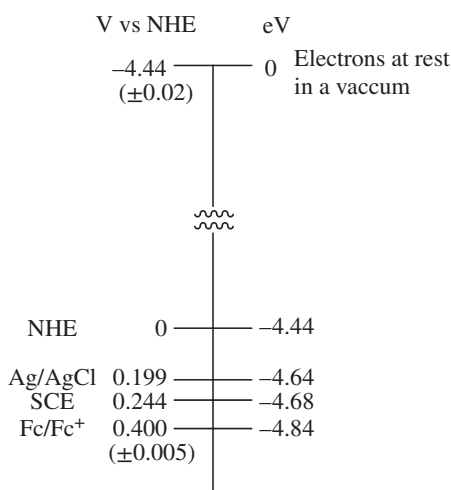


FIGURE 1.1 Conversion of relative electrode potentials into electronic energies for aqueous systems. *Note that this graph cannot be used to convert SCE or Ag/AgCl scale into Fc/Fc⁺ scale in the electrochemical measurements performed in nonaqueous media.*

(solvent polarity, electrolyte, surface of Ag, etc.), the conversion of the Ag/Ag⁺ scale to SCE or Ag/AgCl scale is not straightforward.

Most organic redox compounds do not dissolve in water, and hence their electrochemical measurements have to be taken in a nonaqueous solvent such as dichloromethane, DMF, and acetonitrile. In the case of the use of Ag/Ag⁺ reference electrode in a polar organic solvent, a careful preparation of the reference electrode is required for the reproducible measurements. If an SCE or saturated Ag/AgCl electrode is used as reference, liquid junction potential [13] generated between the aqueous media in reference electrode and the organic solvent used in the measurement cell cannot be negligible. Liquid junction potential causes a shift in the observed value from the inherent redox potential. The liquid junction potentials between saturated aqueous KCl solution and various aprotic polar organic solvents were shown to be 100–200 mV [14]. Occasionally, liquid junction potential exceeds 200 mV [13].

For this reason, IUPAC recommends the use of ferrocene/ferrocenium couple as internal reference for electrochemical measurements in a nonaqueous medium and also to report the potential in the scale against the redox potential of ferrocene (the abbreviation for the potential as V vs Fc/Fc⁺) [15]. The observed potential of Fc/Fc⁺ couple in various solvents and supporting electrolytes using an SCE reference electrode were reported [16]. The selected data are shown in Table 1.1. The observed values both in tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) and perchlorate (TBAClO₄) electrolytes tend to increase with decreasing solvent polarity. The liquid junction potential between aqueous media in the SCE reference electrode and the organic solvents is involved in the observed difference in the potentials for the Fc/Fc⁺ couple. Therefore, care must be taken when comparing the reported data in SCE or Ag/AgCl scale measured in different solvents. It is important to understand that such a comparison involves an unknown potential shift caused by liquid junction potential. Nevertheless, because of reproducibility of an SCE reference electrode even in nonaqueous media, the potentials in Table 1.1 can be used for the conversion from SCE scale to Fc/Fc⁺ scale, when the measurement conditions (solvent and supporting electrolyte) are identical [16].

The HOMO and LUMO levels of organic redox compounds are often estimated from the oxidation (E^{ox} V vs Fc/Fc⁺) or reduction (E^{red} V vs Fc/Fc⁺) potential obtained

TABLE 1.1 Formal Potentials (V) for the Ferrocene/Ferrocenium Couple vs SCE [16]

Solvent	TBAPF ₆	TBAClO ₄
CH ₃ CN	0.40	0.38
DMF	0.45	0.47
CH ₂ Cl ₂	0.46	0.48
THF	0.56	0.53
Other		
H ₂ O (0.1 M NaF)	0.16	

from electrochemical measurements and the energy level of Fc/Fc⁺ couple to vacuum ($E_{\text{Fc/Fc}^+}$ V(abs)) by Equations (1.1) and (1.2) as follows:

$$E_{\text{HOMO}} = -(E^{\text{ox}} + E_{\text{Fc/Fc}^+}) \text{ (eV)} \quad (1.1)$$

$$E_{\text{LUMO}} = -(E^{\text{red}} + E_{\text{Fc/Fc}^+}) \text{ (eV)} \quad (1.2)$$

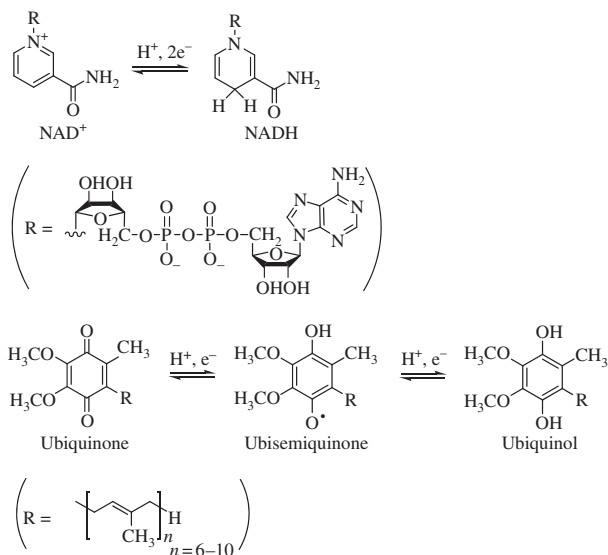
For the $E_{\text{Fc/Fc}^+}$ value, 4.8 eV is frequently used. The value was originally reported in 1995 [17] based on rather crude approximation that the absolute electrode potential for NHE was -4.6 V (the data from an older book) and that redox potential of Fc/Fc⁺ couple was 0.2 V vs NHE in acetonitrile (which is not consistent with the later value shown in Table 1.1). Then, the problems of the rough estimation were raised in 2011 [18].

If 0.40 V vs SCE for the redox potential of Fc/Fc⁺ couple in acetonitrile and TBAPF₆ electrolyte [16] is used under neglecting solvent and electrolyte effects including liquid junction potential (i.e., 0.64 V vs NHE using the conversion scale shown in Figure 1.1), the energy level of Fc/Fc⁺ couple is estimated to be -5.1 eV [18] based on the absolute electrode potential -4.44 V vs NHE. Since the liquid junction potential caused by different electrolytes in the same solvent media is usually smaller than that between aqueous and aprotic nonaqueous media [13], 0.400 ± 0.005 V vs NHE for the redox potential of Fc/Fc⁺ couple in aqueous media [19] may give better estimation. In this case, the energy level of Fc/Fc⁺ couple is estimated to be 4.84 ± 0.025 eV ($= (4.44 \pm 0.02) + (0.400 \pm 0.005)$) below the vacuum level (Fig. 1.1; see also Section 11.3). Although difference in solvation of analyte between aqueous and nonaqueous media would cause some shift of the observed potential referred to Fc/Fc⁺ couple, such a shift may be smaller than the shift caused by liquid junction potential. For example, the difference in redox potential of bis(biphenyl)chromium referred to Fc/Fc⁺ couple between in highly polar propylene carbonate (dielectric constant $\epsilon=64$ (H_2O $\epsilon=80$)) and in less polar dichloromethane ($\epsilon=9$) was only 34 mV [15]. In any case, it is encouraged to disclose the method by which HOMO/LUMO energies are estimated [18].

1.3 A BRIEF HISTORY OF ORGANIC REDOX COMPOUNDS

Redox reaction catalyzed by enzyme (oxidoreductase) is one of the important metabolic processes. Apart from cytochrome and ferredoxin bearing iron–porphyrin core and iron–sulfur clusters, transition-metal-free coenzymes, for example, nicotinamide adenine dinucleotide (NAD⁺) and ubiquinone ($n=10$, CoQ10) (Scheme 1.3), play a central role in redox metabolisms. In this context, living organisms have utilized organic redox reaction from time immemorial. Among these coenzymes, NAD⁺ shows one-step two-electron reduction as observed in many organic redox reactions, while ubiquinone shows stepwise one-electron process involving the radical intermediate (ubisemiquinone) [20].

The synthetic organic redox compounds at the early stage were brought about together with pursuing synthetic dyes and medicines. In 1826, Otto Unverdorben



SCHEME 1.3 Redox reactions of transition-metal-free coenzymes.

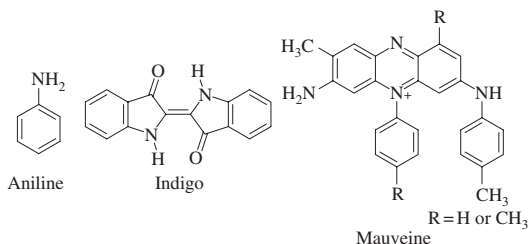


FIGURE 1.2 Structures of aniline, indigo, and mauveine.

isolated aniline for the first time by destructive distillation of natural dye, indigo (Fig. 1.2) [21]. This report was prepared 2 years before Friedrich Wöhler's pioneering discovery in organic chemistry that the organic compound of urea $\text{CO}(\text{NH}_2)_2$ can be synthesized from the inorganic compound of ammonium cyanate NH_4CNO [22]. Then, aniline was obtained by various ways such as distillation from coal tar [23] and reduction of nitrobenzene [24]. However, these products had not been recognized as the same compound, until in 1843 August Wilhelm von Hofmann, who named the term “aromatic” for benzene derivatives, revealed the fact [25]. After the first synthetic dye mauveine, which was accidentally prepared during the attempt synthesis of quinine from aniline by Hofmann's assistant William Henry Perkin in 1856 [26, 27], various synthetic dyes were prepared from aniline and related derivatives.

Thus, radical cation of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD (Fig. 1.3), $E_{1/2}^{\text{ox1}} = -0.27\text{V}$ vs Fc/Fc^+ , $E_{1/2}^{\text{ox2}} = 0.33\text{V}$ in CH_3CN) [28] known as Wurster's blue was isolated in 1879 [29]. As a related compound derived from aniline, methylene blue,

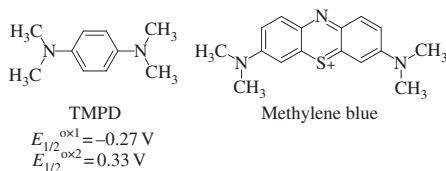


FIGURE 1.3 Structures of TMPD and methylene blue. The redox potentials are vs Fc/Fc^+ .

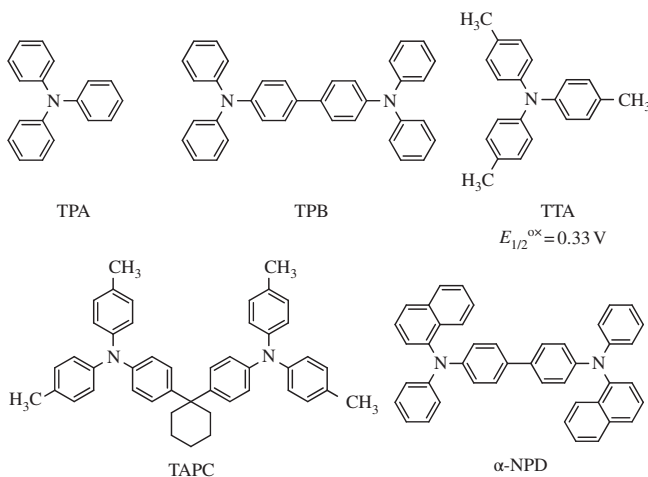


FIGURE 1.4 Structures of triarylamines. The redox potential is vs Fc/Fc^+ .

which is a well-known redox indicator [30] and the first synthetic medicine [31], was prepared 3 years earlier than Wurster's salts in German chemical company BASF (Badische Anilin und Soda-Fabrik (English: Baden Aniline and Soda Factory)). However, methylene blue shows one-step two-electron reduction [30] and does not generate an open-shell species in aqueous media.

Other anilines that give stable radical cations are triarylamines. Synthesis of neutral triphenylamine (TPA; Fig. 1.4) was reported in 1873 [32]. Although radical cation of TPA immediately gives tetraphenylbenzidine (TPB) via radical coupling followed by deprotonation [33], the isolation of radical cation salt of its *p*-methyl derivative (tritolylamine (TTA), $E_{1/2}^{\text{ox1}} = 0.33 \text{ V}$ vs Fc/Fc^+ in CH_2Cl_2) [34] was reported in 1907 [35]. Because of the stability at the oxidized state, various derivatives of triarylamines radical cations are used for oxidizing reagents [16]. Furthermore, their amorphous nature due to the conformational flexibility of triarylamines moiety is advantageous when preparing pinhole-less thin film [36] that is an important prerequisite for the electronic devices. Thus, triarylamines derivatives such as 4,4'-cyclohexylidenebis[*N,N*-bis(4-methylphenyl)aniline] (TAPC) and *N,N'*-bis-(1-naphthalenyl)-*N,N'*-bis-phenyl-(1,1'-biphenyl)-4,4'-diamine (α -NPD) are commonly used as charge transport materials for organic photoconductors (OPCs) [37] and organic electroluminescence (OEL) [38, 39].

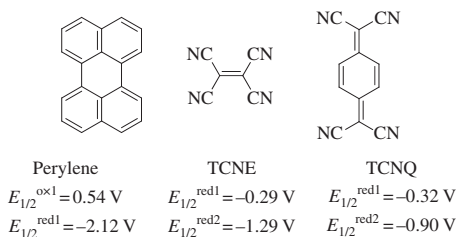
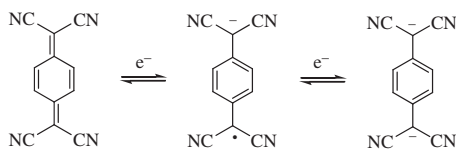


FIGURE 1.5 Structures of perylene, TCNE, and TCNQ. The redox potentials are vs Fc/Fc^+ .

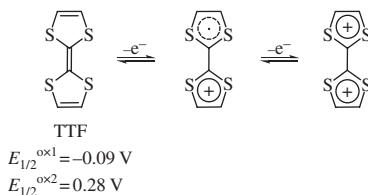


SCHEME 1.4 Redox reactions of TCNQ.

Many aromatic hydrocarbons react with alkali metals to give relatively stable radical anion in ethereal solutions. For example, Na-naphthalene [40] can be handled at room temperature and are often used as reducing reagents. Stable radical cation of some aromatic hydrocarbons such as perylene (Fig. 1.5; $E_{1/2}^{\text{ox}1} = 0.54 \text{ V}$ vs Fc/Fc^+ , $E_{1/2}^{\text{red}1} = -2.12 \text{ V}$ in CH_3CN) [41] can be generated in concentrated sulfuric acid [42], although radical cation of smaller aromatic hydrocarbons are not stable enough. In 1954, Hideo Akamatsu and Hiroo Inokuchi demonstrated that charge transfer complex of perylene with bromine showed high conductivity up to 1.3 S cm^{-1} [43]. Before the study, organic compounds were regarded as insulator. However, this discovery opened the research field of molecular conductors and stimulated the development of various organic acceptors and donors.

Initially, various strong acceptors such as tetracyanoethylene (TCNE, $E_{1/2}^{\text{red}1} = -0.29 \text{ V}$ vs Fc/Fc^+ , $E_{1/2}^{\text{red}2} = -1.29 \text{ V}$ in DMF) [16, 44] and tetracyanoquinodimethane (TCNQ, $E_{1/2}^{\text{red}1} = -0.32 \text{ V}$ vs Fc/Fc^+ , $E_{1/2}^{\text{red}2} = -0.90 \text{ V}$ in DMF) [16, 44] were synthesized [45, 46] in DuPont from late 1950s to mid-1960s after the commercial success of Teflon (polytetrafluoroethylene, PTFE) from mid-1940s. For TCNQ, aromatization plays an important role in the reversible two-step one-electron reduction at lower potentials (Scheme 1.4) in a similar manner to ubiquinone (Scheme 1.3).

As for the donor related to molecular conductors, tetrathiafulvalene (TTF, $E_{1/2}^{\text{ox}1} = -0.09 \text{ V}$ vs Fc/Fc^+ , $E_{1/2}^{\text{ox}2} = 0.28 \text{ V}$ in benzonitrile) [47] is most important. Although the mixture of dimethyl and diphenyl derivatives of TTF were reported in 1965 [48], and even the parent TTF appeared in a dissertation of Würzburg University in 1968 [49], the broad interest arose after the report of the synthesis in 1970 [50] and the metallic conduction of TTF–TCNQ in 1973 [51]. Similar to TCNQ, good donor ability of TTF is partly owing to aromatization from dithiolyldiene to dithiolium moiety upon the oxidation process (Scheme 1.5). In a TTF–TCNQ crystal, partial electron transfer occurs from TTF to TCNQ which forms segregated columnar stacks.



SCHEME 1.5 Redox reactions of TTF. The redox potentials are vs Fc/Fc^+ .

Therefore, holes and electrons are separated and can traverse in a one-dimensional direction along the TCNQ and TTF columns, respectively. Since then, numerous investigations have been carried out to develop molecular conductors [52] and supramolecular systems [53] based on TTF and related molecules. As a result, the first superconductors based on organic radical salts were observed in $(\text{TMTSF})_2\text{PF}_6$ (TMTSF tetramethyltetraselenafulvalene) at 0.9 K and 6.9 kbar [54].

In 1976, Hideki Shirakawa revealed in Alan Graham MacDiarmid laboratory that positively doped polyacetylene with halogen vapor shows high conductivity [55]. The discovery of conducting polymer, awarded with Nobel Prize in Chemistry 2000, had an impact in the field of organic electronic materials. For example, in 1981, a prototype cell using polyacetylene for negative electrode with a LiCoO_2 -positive electrode was fabricated, which led to the birth of the current lithium-ion battery by using carbonaceous material into which lithium ions can be intercalated [56]. In the negative electrode, reduction and oxidation of electrode materials occurs during charging and discharging processes, respectively. The application of some organic and organo main group compounds to the electrodes in secondary batteries is presented in this book (see Chapters 4 and 6). As another application of conducting polymers, the first organic field-effect transistor based on polythiophene was reported in 1986 [57]. Then, oligothiophene and other conjugated polymers and oligomers have been shown to have semiconducting properties. Enormous organic semiconductors for field effect transistors have been reported and reviewed [58–62]. Some examples are also shown in this book (see Chapters 10, 11, 13, and 14).

The discovery of C_{60} and fullerenes in 1985 [63], which was awarded with Nobel Prize in chemistry 1996, and carbon nanotubes in 1991 [64], further pushed the development of carbon-based electronic devices. C_{60} shows reversible multistep one-electron oxidations as well as reductions ($E_{1/2}^{\text{ox1}} = 1.26 \text{ V}$ vs Fc/Fc^+ , $E_{1/2}^{\text{ox2}} = 1.71 \text{ V}$, $E_{1/2}^{\text{red1}} = -1.06 \text{ V}$, $E_{1/2}^{\text{red2}} = -1.46 \text{ V}$, $E_{1/2}^{\text{red3}} = -1.89 \text{ V}$, in CH_2Cl_2), when weakly nucleophilic anion AsF_6^- is used as electrolyte in CV measurement (Fig. 1.6) [65]. Concerning the conductive properties of these carbon materials, superconductivity was observed for K_3C_{60} in 1991 [66]. All armchair nanotubes are metallic, while other chiral nanotubes are semiconducting [67]. Thus, to understand and utilize these unique electronic properties, various fragments of fullerenes and nanotubes have also been synthesized. Since the topic has been summarized in one of the recent books published by Wiley [68], most of it will not be covered here, but a model system of graphene sheet and other unique hydrocarbon systems are introduced in this book (see Chapters 6, 9, and 10).

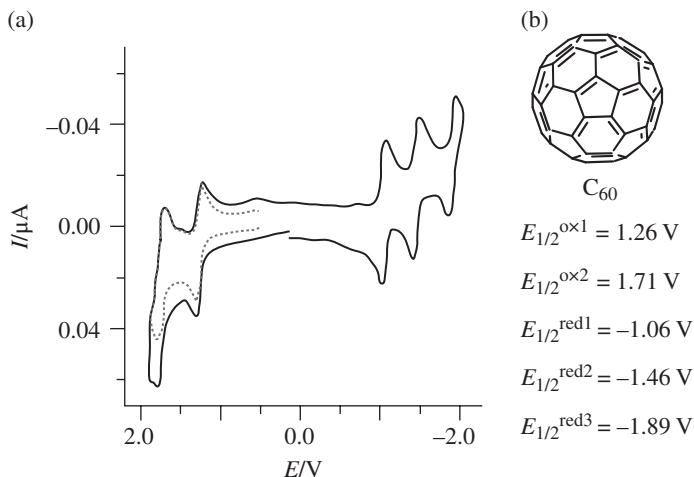


FIGURE 1.6 (a) Cyclic voltammogram of 0.15 mM C_{60} in 0.05 M TBAAFs₆ CH_2Cl_2 solution. Working electrode: Pt disk (125 μ m diameter). Scan rate: 1 V/s. $T=25^\circ C$. Dashed curve: as solid curve after background current correction. Reprinted with permission from Ref. 65. © 2003 American Chemical Society. (b) Drawing of C_{60} . The redox potentials are vs Fc/Fc^+ .

In summary, organic redox systems have been developed in relation to the application of organic materials to functional dyes and electronic devices. The emerging interest in organic materials will further advance the development of organic redox systems and deepen the knowledge of their various properties such as electronic state and bonding interaction between stable radicals, magnetism, and conductivity.

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