

JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 102, NUMBER 17

AUGUST 13, 1980

Electrochemical Behavior of Donor-Tetracyanoquinodimethane Electrodes in Aqueous Media

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Abstract: Electrodes prepared as compacted pellets from conductive donor-acceptor complexes of tetracyanoquinodimethane (TCNQ) with several donors (D) (tetrathiotetracene, acridine, quinoline, *N*-methylphenazine, 2,2'- and 4,4'-bipyridine) were investigated in aqueous solutions. The results were compared to those of a previous investigation of TTF-TCNQ pellets (TTF = tetrathiafulvalene) and to results on single crystals of TTF-TCNQ reported here. The electrodes are stable over a potential region in which they could be employed as inert electrodes. The potential limits depended upon the stabilization gained upon complexation and the relative electrode potentials of the constituent compounds. Upon exceeding the potential limits of stability of the electrode, the electrode was reduced or oxidized. Subsequent voltammograms showed peaks attributable to insoluble compounds formed on the electrode surface. The potentials observed for the redox processes could be correlated to the degree of charge transfer, ρ , as well as gas-phase ionization potentials and electron affinities.

Introduction

Hundreds of different molecular complexes containing tetracyanoquinodimethane (TCNQ) as the acceptor have been made.¹⁻⁴ TCNQ is a very good electron acceptor; because of the presence of the four cyano groups on the molecule and the relatively large π conjugation system, reduction to the radical anion occurs very easily. As a result, TCNQ forms stable solid complexes with a wide variety of electron-donating compounds. Because of their special structural features, some of these complexes exhibit the highest conductivity observed for organic compounds. The structure of the donor, the stoichiometry, and the electrical conductivity for some of these highly conducting donor-TCNQ complexes are shown in Figure 1. Donor-acceptor complexes of intermediate ($10^{-4} \Omega^{-1} \text{ cm}^{-1}$) and very low ($10^{-9} \Omega^{-1} \text{ cm}^{-1}$) conductivity also exist. TCNQ forms three types of complexes with donor molecules.¹ The first can be generally characterized as π molecular complexes with relatively low electrical conductivities. The second group includes the simple radical ion salts, $M^{n+}TCNQ^{\cdot-}$, where M^{n+} can be either a metal cation or an organic cation. The third type includes the complex (1:2) radical ion salts, $M^+(TCNQ^{\cdot-})_2(TCNQ^0)$. In these complexes the electron is generally considered to be delocalized over both of the TCNQ molecules.

Although the properties and synthesis of these materials have been investigated quite extensively, few reports on the application

of such donor-acceptor complexes have appeared. We recently discussed the behavior of sintered pellets of TTF-TCNQ as electrodes.^{5,6} These were shown to have a stable region where they behaved as inert electrodes capable of carrying out electrochemical reactions of dissolved solution species without oxidation or reduction of the electrode material itself. Outside of this region different reactions of the electrode occurred that depended upon the nature of the supporting electrolyte in the solution. In this paper these studies are extended to single-crystal TTF-TCNQ and a number of other donor-TCNQ complexes. Such studies are of interest because they provide information about the redox behavior, stabilization energies, and degree of charge transfer in these complexes. These materials are of potential interest as electrodes for electroanalytical studies or in electrochemical cells and may have application to electrochromic devices.

Experimental Section

Preparation of Complexes and Electrodes. In general most of the complexes cannot be recrystallized without some degradation. Thus they were synthesized with materials of the highest purity. TCNQ and the donor molecules were generally sublimed several times and then recrystallized from a spectroscopic grade solvent (benzene, MeCN). The inorganic salts were similarly recrystallized before they were used in a synthesis. All solvents were spectroscopic grade and the water was triply distilled starting with alkaline potassium permanganate.

TCNQ forms several different types of compounds. They can be simple 1:1 complexes, represented by the formula $D^{n+}(TCNQ^{\cdot-})_n$, or complex salts represented by the formula $D^{n+}(TCNQ^{\cdot-})_n(TCNQ^0)$.^{1,7} In both cases complete and incomplete charge transfer from the donor to

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| DONOR | COMPLEX | $\sigma(\Omega^{-1}\text{cm}^{-1})$ |
|------------------------------------|------------|-------------------------------------|
| tetrathiafulvalinium(TTF) | 1:1 | 300 |
| N-methylphenazinium(NMP) | 1:1 | 140 |
| acridinium(Ad) | 1:2 | 70 |
| quinolinium(Qn) | 1:2 | 100 |
| tetrathiotetracene(TTT) | 1:1 1:2 | 1 100 |
| 2-2' Bipyridinium(2-2' BIP) | 1:2 | 2 |
| 4-4' Bipyridinium(4-4' BIP) | 1:1 | $\sim 10^{-2}$ |
| tetracyanoquinodimethane(TCNQ) | | |

Figure 1. Structures of components of conducting donor-TCNQ complexes (σ data from ref 3).

the TCNQ can occur. The synthesis of these compounds involved three general methods: (1) direct reaction of the donor and TCNQ, (2) reaction of the donor with H_2TCNQ and TCNQ, and (3) metathesis of the donor and TCNQ salts.

The TTF-TCNQ complex was formed by mixing equimolar (~ 0.1 M) hot anhydrous MeCN solutions of neutral TCNQ and TTF. The black complex immediately precipitated as a microcrystalline powder. These crystals were washed with cold MeCN then diethyl ether and finally dried under vacuum. The TTF was synthesized by the procedure of Melby et al.⁸ Other TTF samples were purchased from Aldrich Chemical Co. (Milwaukee, Wis.), as was the TCNQ.

Tetrathiotetracene (TTT) can form both 1:1 and 1:2 complexes with TCNQ.⁹⁻¹² The 1:1 complex was prepared by the complexation of TTT acetate¹³ and LiTCNQ^1 in methanol. The 1:2 complex was prepared by mixing hot nitrobenzene solutions containing stoichiometric quantities of TTT and TCNQ.^{4,9} In both cases, the precipitated salts formed immediately. The powders were filtered and washed with solvent used in the synthesis and then with ether. They were dried in a vacuum desiccator for 24 h. The TTT was synthesized by Marschalk's method.^{14,15}

N-Methylphenazinium (NMP) forms a 1:1 complex with TCNQ.^{16,17} This complex was prepared by mixing equimolar aqueous solutions of NMP⁺ (as phenazine methosulfate, purchased from Aldrich) and TCNQ⁻ (as LiTCNQ). The black precipitate formed after approxi-

mately 20 min. It was filtered, washed with water and ether, and then dried. A new series of complexes have recently been synthesized based on NMP, TCNQ, and phenazine (Phen), $(\text{NMP})_X(\text{Phen})_{1-X}(\text{TCNQ})$ ($1.0 \geq X \geq 0.5$).^{18,19} The NMP molecules can be replaced by Phen up to 50% in the TCNQ complex. Two such complexes ($X = 0.85$ and 0.63) were synthesized. They were prepared by combining hot MeCN solutions containing TCNQ⁰, Phen⁰, Li^+TCNQ^- , and $\text{NMP}^+\text{PF}_6^-$ in the appropriate mole ratios.¹⁸ Dark crystals formed after about 2 h. They were then filtered, washed with MeCN and ether, and dried. The Phen was purchased from Aldrich and the $\text{NMP}^+\text{PF}_6^-$ was prepared by mixing aqueous solutions of phenazine methosulfate and sodium hexafluorophosphate.

A 1:2 TCNQ complex was formed with acridine (Ad). Two methods were used to prepare this complex. In the first stoichiometric amounts of acridine hydrochloride (purchased from Aldrich), LiTCNQ , and LiI were mixed in aqueous solutions.²⁰ This method proved generally unacceptable because of the coprecipitation of some unknown substance as well as the presence of I_2/I^- in the solution. The preferred method involved the reaction of acridine (Ad) (purchased from Aldrich), H_2TCNQ , and TCNQ in hot MeCN. A dark, fibrous precipitate formed as the solution cooled. It was filtered, washed with MeCN and then ether, and dried overnight. The H_2TCNQ was prepared by adding excess thiophenol to a glacial acetic acid solution of TCNQ.²¹ The H_2TCNQ formed was a white, crystalline powder.

Quinoline (Qn) (refined, Matheson Coleman and Bell), H_2TCNQ , and TCNQ were mixed in stoichiometric quantities, using hot MeCN, to form a 1:2 complex.¹ This complex immediately formed as a dark precipitate. It was filtered, washed with MeCN and ether, and then dried.

By the same method as above, 2,2'-bipyridine (purchased from G. Frederick Smith Chemical) or 4,4'-bipyridyl dihydrate (purchased from Aldrich), H_2TCNQ , and TCNQ were combined to form a 1:2 complex.¹ A number of bipyridinium complexes could be formed, particularly derivatives of 4,4'-bipyridinium. These complexes were prepared by reacting solutions of the dication bromide or chloride salts of bipyridine with stoichiometric amounts of TCNQ and LiTCNQ .²²

The preparation of the metal complexes and several other complex salts followed previous methods.¹ Generally, the preparations were carried out by combining the donor and TCNQ directly or by metathesis of the cation source with LiTCNQ . In addition to the materials discussed above, single crystals of a TCNQ complex with trimethylammonium iodide [$(\text{NMe}_3\text{H})(\text{I})\text{TCNQ}$ and $(\text{NMe}_3\text{D})(\text{I})\text{TCNQ}$] were provided by A. J. Epstein and J. S. Miller.^{23,24}

The donor-TCNQ complexes were fabricated into flat disks 0.5–1.0 mm thick, by pressing the microcrystalline powder in a 10-mm diameter die at a pressure of 2500–3000 psi. The disks thus formed had a mirror-like appearance. The resistance of the electrode was determined by forming a contact on both sides of the disk as described below. Contacts were made to the disks by connecting a copper wire to one side with conducting silver epoxy (Allied Products Corp., New Haven, Conn.). An ohmic contact was confirmed by making a second contact to the other side of the selected disks. In all cases the contact resistance was small and the current was directly proportional to the applied voltage. The back and sides of the electrode and the attached wire were sealed with nonconducting 5-min epoxy cement (Devcon Corp., Danvers, Mass.). The disks were then mounted on a glass tube and sealed to the glass with silicone adhesive (Dow Corning, Midland, Mich.), leaving exposed a flat, shiny portion of the surface with electrode areas typically 0.1–0.2 cm^2 . Larger single crystals of TTF-TCNQ were formed by allowing MeCN solutions of the neutral species to diffuse together over a period of several weeks at a temperature of about 30 °C. Several other single crystals of TTF-TCNQ were also provided by F. Wudl. These single crystals were fairly long, narrow, and flat needles ($4 \times 1 \times 0.1$ mm). Contacts were made to one of the flat sides in the same manner as for the pressed disks. Thin films of TTF-TCNQ were formed on conducting SnO_2 glass by vacuum deposition techniques. Electrical contact was made to the SnO_2 conducting glass.

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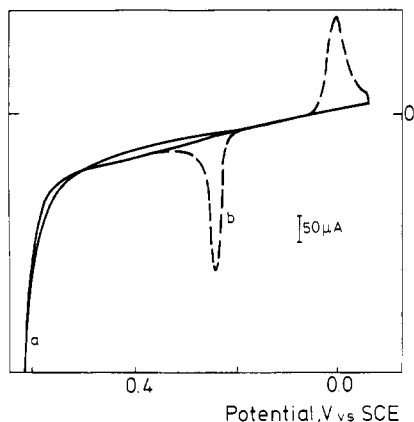


Figure 2. Cyclic voltammogram of a TTF-TCNQ (single crystal) electrode, 1 M KCl: (a) —, stable potential region and oxidation of lattice; (b) ---, peaks on reversal scans resulting from the oxidation of the electrode.

The electrochemical apparatus and experimental procedures were the same as those previously described.⁵

Results

Tetrathiafulvalene (TTF)-TCNQ. Previous investigations of TTF-TCNQ electrodes have involved compressed disks.⁵ For comparative purposes several studies of single-crystal and thin-film TTF-TCNQ electrodes were carried out. There were no significant differences between compressed-disk, single-crystal, and thin-film electrodes of TTF-TCNQ. The single-crystal electrodes sometimes showed somewhat larger background current densities in the stable region (Figure 2), which probably resulted from difficulties in making good electrical contact to the crystal. As with compressed pellet electrodes, when the potential scan was made to potentials beyond 0.6 V vs. SCE, lattice oxidation occurred. This resulted in a layer of TCNQ⁰ being formed on the electrode surface.⁵ Peaks for the reduction and oxidation of this substance appeared on subsequent scans (Figure 2, curve b). For the compressed-disk electrodes, the integrated peak areas depended upon the extent of lattice oxidation and reduction and corresponded to quantities of electricity of 20 to over 100 mC/cm² projected area (as opposed to the ~40 μC/cm² expected for a monolayer process). This was attributed to multilayer decomposition of the TTF-TCNQ lattice with replacement of TTF⁺ by K⁺, although it was possible that the results could be caused by porosity of the sintered electrode material and surface roughness.⁵ However, the studies with single-crystal TTF-TCNQ electrodes clearly demonstrate that the number of coulombs consumed during the various faradaic processes represent multilayer (i.e., >100 monolayers) oxidation and reduction. A TTF-TCNQ single crystal electrode (*A* ≈ 0.05 cm²) in 1 M potassium acetate consumed 2.9 mC during lattice oxidation. Subsequent scans involving the TCNQ⁰/K⁺TCNQ⁻ couple still consumed ~1 mC. Thus the multilayer redox processes and ion replacement mechanism previously proposed appear valid.

The results for the donor-TCNQ complexes presented in the following sections employ compressed-disk electrodes. So that these results can be compared more easily to those found for the TTF-TCNQ electrode, a cyclic voltammogram of a TTF-TCNQ electrode in 1 M KBr is presented (Figure 3).⁵ In this case, the salts formed on the electrode surface (e.g., M⁺TCNQ⁻ or TTF⁺X⁻) following lattice oxidation or reduction are insoluble. Such peaks, which can be attributed to the TCNQ⁰/M⁺TCNQ⁻ couple, can be observed for all donor-TCNQ electrodes.

Tetrathiotetracene (TTT)-TCNQ_n. Tetrathiotetracene (TTT), like TTF, is a good donor with halogens and related compounds, and forms highly conducting compounds with these acceptors, TTTX_n,^{25,26} and also conducting 1:1 and 1:2 complexes with

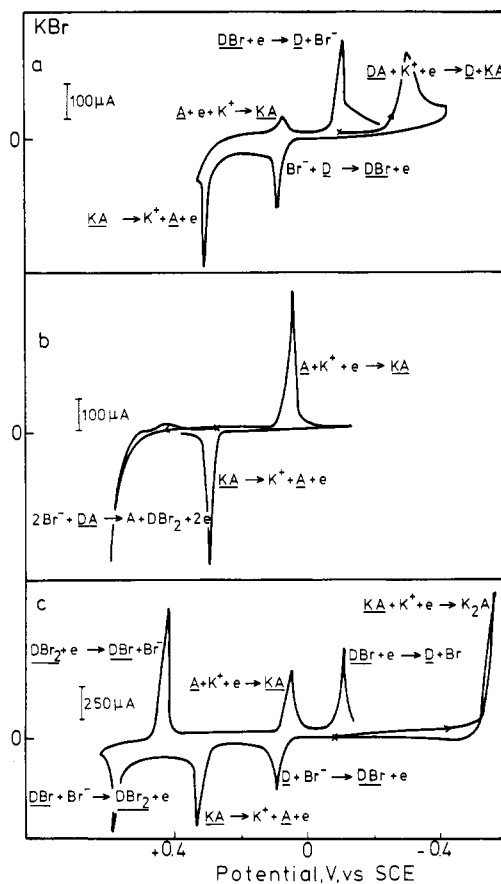


Figure 3. Cyclic voltammogram of the TTF-TCNQ electrode in 1 M potassium bromide: (a) initial negative scan with reduction of the electrode surface and resultant peaks on reversal; (b) initial positive scan with oxidation of the electrode surface and resultant peaks on reversal; (c) after the electrode surface has been oxidized and reduced. Scan rate, 5 mV/s. A and D represent TCNQ and TTF, respectively. Insoluble or slightly soluble species are underlined. Scans start at potential marked by X.

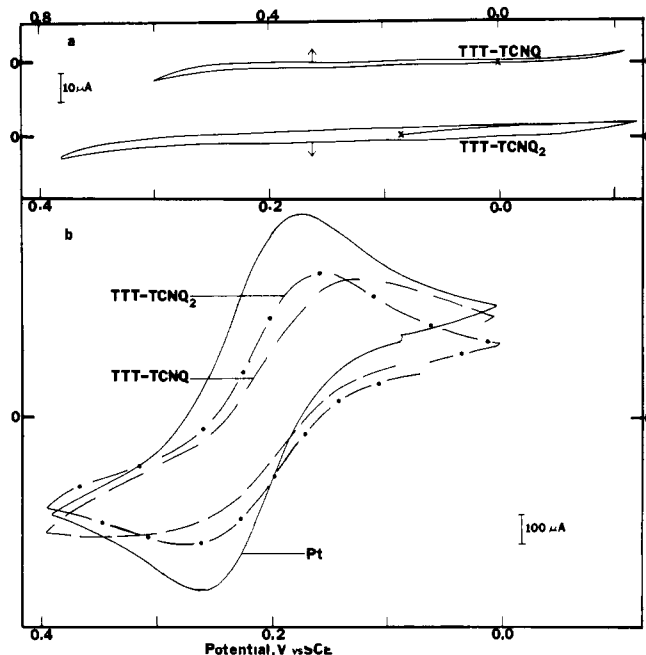


Figure 4. (a) Stable potential region for TTT-TCNQ and TTT-TCNQ₂ electrodes in a HAc/KAc buffer solution (pH 6.9), 10 mV/s scan rate. (b) Cyclic voltammogram of 10 mM K₃Fe(CN)₆/K₄Fe(CN)₆ in HAc/KAc (pH 6.9) solution, 10 mV/s scan rate. (1) Pt electrode, (2) TTT-TCNQ electrode, (3) TTT-TCNQ₂ electrode.

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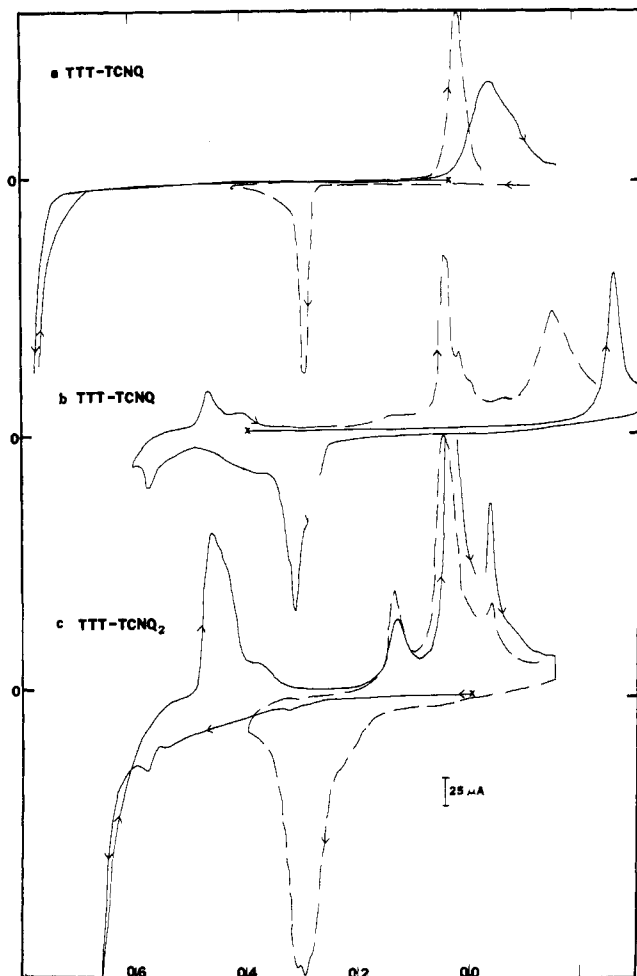


Figure 5. (a) Lattice oxidation of a TTT-TCNQ electrode in 1 M KAc. (b) Lattice reduction of a TTT-TCNQ electrode in 1 M KCl. (c) Lattice oxidation of a TTT-TCNQ₂ electrode in 1 M KCl. Scan rate, 5 mV/s.

TCNQ.^{4,10-12} The cyclic voltammograms of both TTT-TCNQ_n complexes show a stable potential region (Figure 4a). The 1:1 complex has a more positive potential limit than both the 1:2 complex and the TTF-TCNQ electrode. For both electrodes redox species in solution can be oxidized or reduced within this potential region with no change in the electrode itself (Figure 4b). Upon exceeding the potential limits, the electrodes are oxidized or reduced, and on subsequent scans peaks are observed which can be attributed to species formed on the surface. As with TTF, the TTT acetate salt is soluble in aqueous media. Thus the oxidation and subsequent scans of the TTT-TCNQ electrode in 1 M KAc appear very similar to those of the TTF-TCNQ electrode.

The assignment of the reactions which occur at the different peaks was made following the same procedures described for TTF-TCNQ.⁵ The material formed on the electrode surface upon lattice oxidation is TCNQ⁰. This species is subsequently reduced at 0.02 V vs. SCE, forming KTCNQ on the surface. Upon lattice reduction of TTT-TCNQ and TTT-TCNQ₂ electrodes in 1 M KCl (Figure 5b,c), in addition to the peaks which can be attributed to TCNQ, peaks caused by formation of TTTCl_n salts are also observed. Although similar behavior is observed for TTF-TCNQ,⁵ the TTTCl_n peaks are larger and more stable than the TTFCl_n salts formed during lattice oxidation. This may be due, in part, to the lower solubility of TTT and some of the TTT salts in aqueous media.

***N*-Methylphenazinium (NMP)-TCNQ.** NMP-TCNQ belongs to the class of 1:1 TCNQ complexes which show incomplete charge transfer, NMP^{0.94}+TCNQ^{0.06}- ($\rho = 0.94 \pm 0.05$).²⁷ One might expect

that TCNQ^{0.94}- would be more easily oxidized than TCNQ^{0.59}- (as found in the TTF-TCNQ complex). Indeed, as shown in Figure 6a, the anodic current for lattice oxidation begins at about +0.2 V vs. SCE (compared to ~0.5 V for the TTF salt). Again TCNQ⁰ is formed on the electrode surface and can be subsequently reduced, resulting in a KTCNQ layer. The reduction of the NMP-TCNQ lattice (Figure 6b) occurs at more negative potentials than for TTF-TCNQ, with the production of a reduced NMP species and KTCNQ on the electrode surface. The nature of the reduced NMP species is unknown; all subsequent references to NMP⁰ denote such a species. The very small stable potential region for the NMP-TCNQ electrode reduces the usefulness of this complex as an inert electrode. However, as shown in Figure 6c, copper can be deposited and then anodically stripped from the electrode without changing the surface.

The substitution of phenazine, Phen⁰, for NMP⁺ in the NMP-TCNQ complexes has been claimed to reduce the number of electrons on the TCNQ stack.^{18,19} Thus, as the negative character of TCNQ is made smaller (i.e., the degree of reduction of TCNQ⁰ to TCNQ⁻ is reduced to $\rho \sim 0.85$ or 0.63), oxidation of this species should be more difficult. Again the cyclic voltammetry of the two NMP_xPhen_{1-x}TCNQ ($x = 0.85$ and 0.63) complexes (Figure 7) supports this expectation. As before TCNQ⁰, formed on the electrode surface during the oxidation, is reduced to KTCNQ on scan reversal.

Acridinium (Ad)-TCNQ₂. Acridinium cations form highly conducting quasi-one-dimensional complexes with TCNQ ($170 \Omega^{-1} \text{ cm}^{-1}$)²⁸ with a stoichiometry of 1:2. The cyclic voltammograms for the Ad-TCNQ₂ electrode (Figure 8) again show a stable potential region (ca. +0.55 to -0.25 V vs. SCE) in which solution species, e.g., 10 mM K₃Fe(CN)₆/K₄Fe(CN)₆, can be examined. The general behavior of this electrode is similar to that of TTF-TCNQ. The oxidation of the lattice (Figure 8) results in the formation of TCNQ⁰ on the surface ($E = 0.57$ V vs. SCE). The formation of insoluble chloride salts with the Ad cation does not occur upon lattice oxidation and no conducting Ad salts (i.e., AdX_n, where X = Cl⁻, Br⁻, or I⁻) have been reported. Lattice reduction in KBr (Figure 8c) results in the formation of KTCNQ. The oxidation of the resulting KTCNQ requires about one-half of the number of coulombs consumed during lattice reduction. If Ad is formed during this process, either it dissolves into the solution (Ad is known to be slightly soluble in hot water),²⁹ its reduction is irreversible, or Ad is oxidized positive of +0.5 V vs. SCE. No products are formed during the oxidation of acridine ($E_{p/2} = 1.58$ V vs. SCE, in MeCN) which are electroactive positive of -0.5 V vs. SCE.³⁰

Quinolinium (Qn)-TCNQ₂. Qn-TCNQ₂ is a highly conducting quasi-one-dimensional TCNQ complex salt ($100 \Omega^{-1} \text{ cm}^{-1}$)^{28,31,32} in which the TCNQ units are stacked in columns with the average spacing intermediate between those of TCNQ⁰ and TCNQ⁻.³³ Lattice oxidation occurs at less positive potentials than for the TTF, TTT, and Ad TCNQ complexes (Figure 9); as before, TCNQ⁰ is formed on the electrode surface. No other electroactive oxidation products are observed. Another feature of the Qn-TCNQ₂ electrochemical behavior is the presence of peak A on

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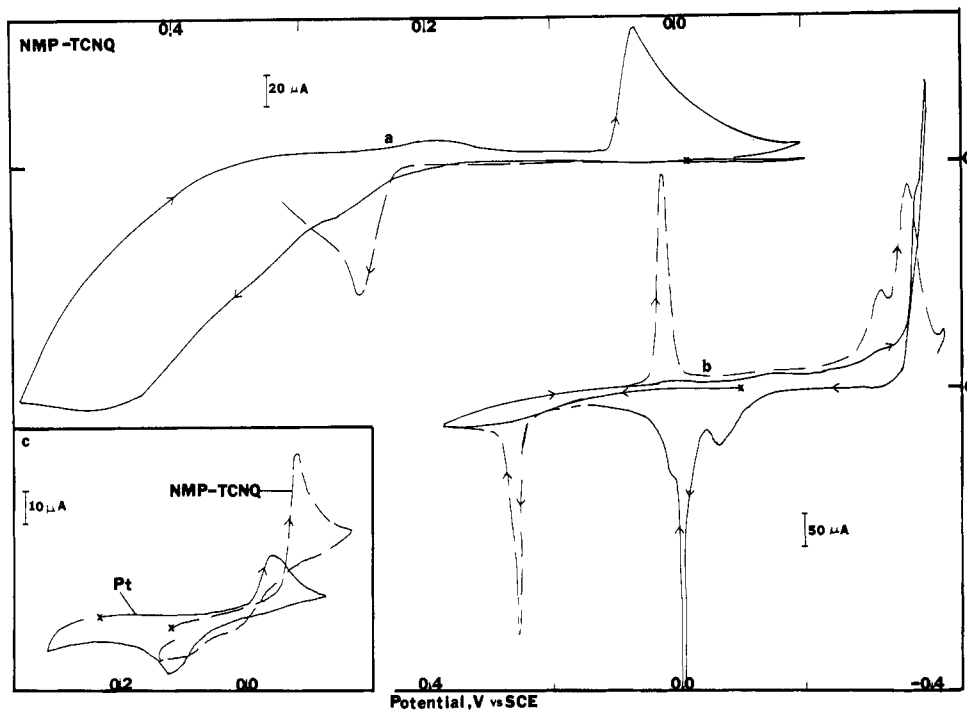


Figure 6. (a) Lattice oxidation of a NMP-TCNQ electrode in 1 M KCl, 2 mV/s scan rate. (b) Lattice reduction of a NMP-TCNQ electrode in 1 M KAc, 5 mV/s scan rate. (c) Deposition of Cu^0 on a Pt and NMP-TCNQ electrode, 20 mM CuSO_4 in 1 M KAc, 5 mV/s scan rate.

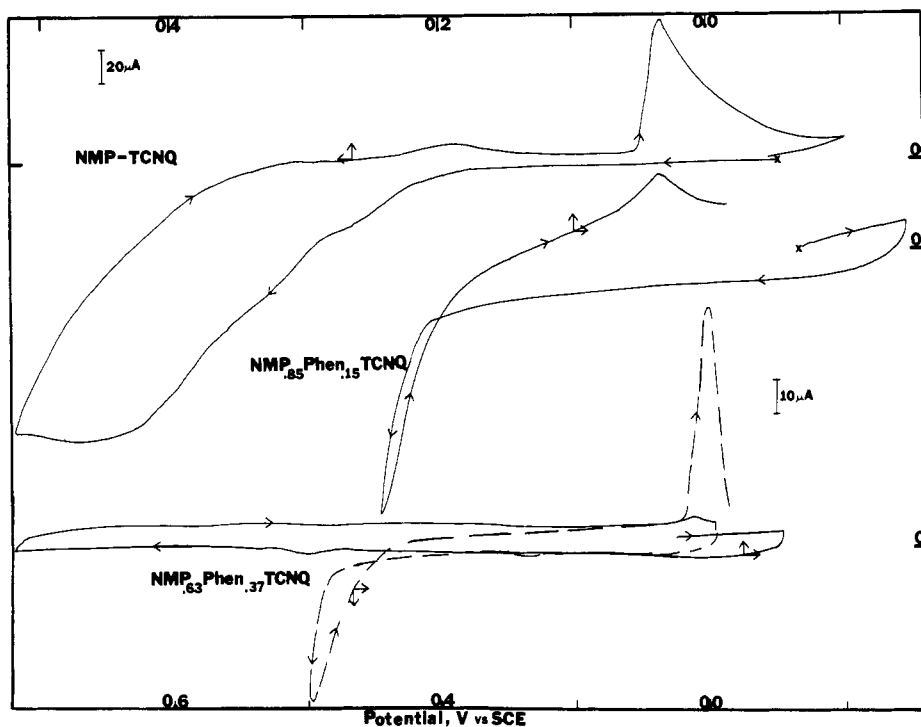


Figure 7. Lattice oxidation of NMP-TCNQ and NMP(Phen_{1-x})TCNQ electrodes, 1 M KCl, 5 mV/s scan rate: (a) NMP-TCNQ electrode; (b) $\text{NMP}_{0.85}\text{Phen}_{0.15}\text{TCNQ}$ electrode; (c) $\text{NMP}_{0.63}\text{Phen}_{0.37}\text{TCNQ}$ electrode.

initial scans toward positive potentials (Figure 9). This peak corresponds to the oxidation of TCNQ^- to TCNQ^0 and was present to a varying extent in all Qn-TCNQ₂ electrodes studied. Although the complex salts of TCNQ are sometimes considered as a mixture of TCNQ^0 and TCNQ^- , the electron is delocalized over the entire TCNQ column. However, this behavior demonstrates that some TCNQ^- was present initially in Qn-TCNQ₂. The presence of this small anodic peak (A) is not unique to the Qn-TCNQ₂ electrode and it may, in fact, be due to some lattice decomposition under open-circuit conditions.

Bipyridinium (BIP)-TCNQ₂. A number of bipyridine-TCNQ salts can be prepared.^{1,22} The 1:2 complex 2,2'-bipyridine

(2,2'-BIP)-TCNQ₂ has a room temperature conductivity greater than $2 \Omega^{-1} \text{cm}^{-1}$, while that of the 4,4'-bipyridine (4,4'-BIP)-TCNQ₂ complex (and other substituted 4,4'-BIP-TCNQ complexes) ranges from 10^{-2} to $10^{-4} \Omega^{-1} \text{cm}^{-1}$.^{1,22}

The 2,2'-BIP-TCNQ₂ electrode in KBr also shows a small anodic peak (A) at -0.27 V vs. SCE at initial scans toward positive potentials (Figure 10). This peak results in the formation of TCNQ^0 on the electrode surface, since the reduction to KTCNQ^- can be observed on scan reversal. Upon cycling between $+0.3$ and -0.04 V the magnitude of the two peaks gradually increased over the first five to six scans. The same behavior was noted for the Qn-TCNQ₂ electrode but not for any other cases discussed

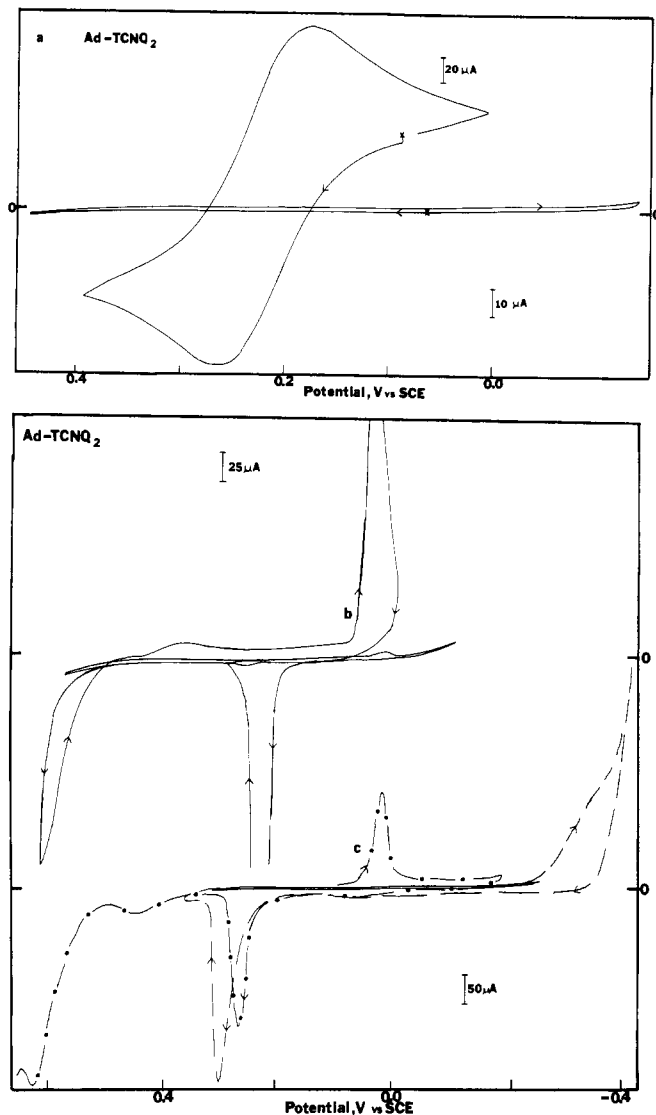


Figure 8. Cyclic voltammograms for a Ad-TCNQ₂ electrode: (a) stable potential region and cyclic voltammogram of 10 mM K₃Fe(CN)₆/K₄Fe(CN)₆ in HAc/KAc solution (pH 6.9); (b) lattice oxidation in 1 M KCl, 5 mV/s scan rate; (c) lattice reduction and subsequent scans in 1 M KBr, 5 mV/s scan rate.

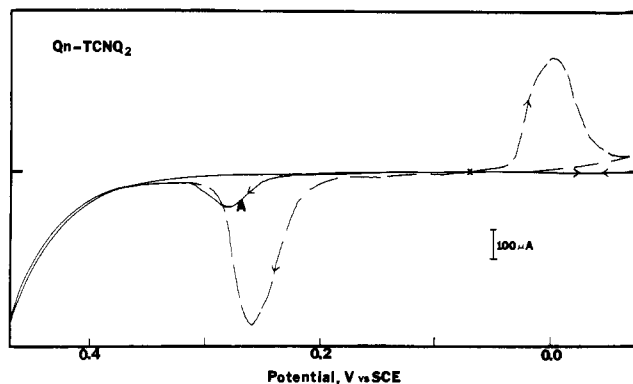


Figure 9. Lattice oxidation of a Qn-TCNQ₂ electrode in 1 M KBr, 10 mV/s scan rate; peak A present on initial scan.

so far. At potentials more positive than +0.4 V, the lattice oxidized, also resulting in TCNQ⁰ on the electrode surface. Only peaks attributable to the TCNQ⁰/TCNQ⁻ couple were observed after lattice oxidation.

The 4,4'-BIP-TCNQ electrode has a much higher resistance than that for the 2,2'-BIP complex (i.e., the *iR* compensation required for the 4,4'-BIP complex was four to five times greater

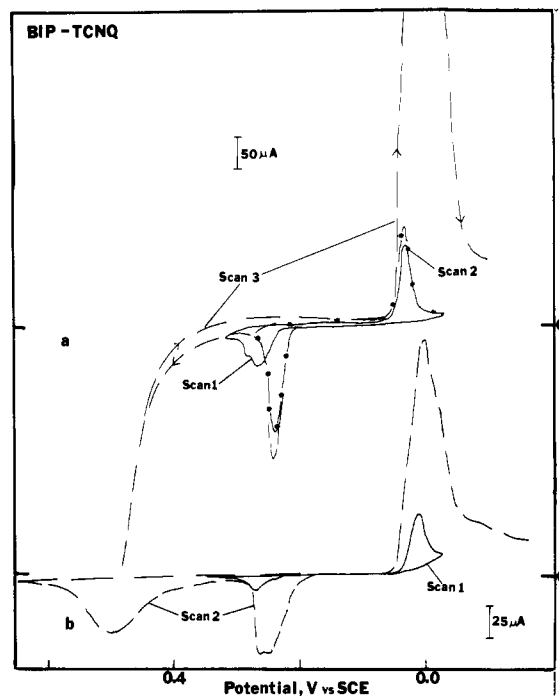


Figure 10. (a) Lattice oxidation of 2,2'-BIP-TCNQ₂ electrode in 1 M KBr. (b) Lattice oxidation of 4,4'-BIP-TCNQ₂ electrode in 1 M KAc, 5 mV/s scan rate.

than that for the 2,2'-BIP complex). Moreover the 4,4'-BIP-TCNQ₂ complex was not stable at open circuit in aqueous solutions. After immersion for about 30 s in a 1 M potassium acetate solution, the dark 4,4'-BIP-TCNQ₂ electrode became purple. The cyclic voltammogram for a 4,4'-BIP-TCNQ₂ electrode showed anodic peaks at +0.25 and +0.50 V (Figure 10b) that can both be attributed to the formation of TCNQ⁰ on the electrode surface. Reduction of the lattice occurred at slightly more negative potentials (~0.4 V vs. SCE) than for TTF-TCNQ.

Metal (Mⁿ⁺)-TCNQ_n. Generally most of the metal TCNQ salts can be represented by the formula Mⁿ⁺TCNQ_n. These show large thermal activation energies for conductivities, which are <10⁻³ Ω⁻¹ cm⁻¹. Because these complexes have complete transfer of one charge from the donor to TCNQ, their potential range appears to be limited by the oxidation of TCNQ⁻ (~0.24 V vs. SCE) and the reduction to TCNQ²⁻ (in a broad cathodic peak starting at about -0.3 V and reaching a limiting current at -0.5 V).

Other TCNQ Complexes. A number of other TCNQ salts exhibit similar electrochemical behavior. For example, ferrocenium-TCNQ₂ behaves very much like the Qn and BIP-TCNQ complexes. However, many other TCNQ complexes (e.g., with the donors *p*-phenylenediamine (PD) and triethylammonium (TEA)) behave like the metal complexes. The highly conducting trimethylammonium iodide-TCNQ complexes were not stable in aqueous media (with KAc, KCl, or LiCl) even at open circuit. Within a few minutes these materials became covered with a yellowish film, probably TCNQ⁰. In addition to the yellow material on the electrode surface (TCNQ⁰) an ammoniacal odor was detected (possibly NMe₃).

Electrochemical Behavior of Some Donor Compounds and TCNQ in Solution. To aid in the discussion of the electrochemical behavior, the redox potentials of the donor and TCNQ couples in solution are listed in Table I. Note that, for those peaks which involve a solid species (i.e., TCNQ⁰, TTF⁰), the peak potentials of the species in solution and those present on the electrode surface are very similar.

Discussion

An interpretation of the processes occurring at various potentials for the different materials generally follows the procedures employed for TTF-TCNQ previously.⁵ Lattice oxidation of the

Table I. Redox Potentials for Donor and TCNQ Couples

| redox couple | E , V vs. SCE | solution | elec- trode | ref |
|---------------------------------------|---------------------|--|----------------|--------------|
| TCNQ ⁰ /TCNQ ⁻ | +0.115 ^a | water/0.1 M LiClO ₄ | Pt | 34 |
| TCNQ ⁻ /TCNQ ²⁻ | -0.133 ^a | water/0.1 M LiClO ₄ | Pt | 34 |
| TCNQ ⁰ /TCNQ ⁻ | +0.127 ^b | MeCN/0.1 M LiClO ₄ | DME | 1 |
| TCNQ ⁻ /TCNQ ²⁻ | -0.291 ^b | MeCN/0.1 M LiClO ₄ | DME | 1 |
| TTF ⁺ /TTF ⁰ | +0.30 ^a | MeCN/0.1 M TEAP | (Pt?) | 35 |
| TTF ²⁺ /TTF ⁺ | +0.66 ^a | MeCN/0.1 M TEAP | (Pt?) | 35 |
| TTF ⁺ /TTF ⁰ | +0.33 ^a | MeCN/0.1 M TEAP | Pt | 36 |
| TTF ²⁺ /TTF ⁺ | +0.70 ^a | MeCN/0.1 M TEAP | Pt | 36 |
| TTT ⁺ /TTT ⁰ | +0.12 ^a | MeCN/0.1 M TEAP | Pt | 35 |
| TTT ²⁺ /TTT ⁺ | +0.49 ^a | MeCN/0.1 M TEAP | Pt | 35 |
| TTT ⁺ /TTT ⁰ | +0.24 ^a | CH ₂ Cl ₂ /TTTCl | Pt | 37 |
| TTT ²⁺ /TTT ⁺ | +0.73 ^a | CH ₂ Cl ₂ /TTTCl | Pt | 37 |
| TTT ⁺ /TTT ⁰ | +0.26 ^a | water/HAc, KAc | glassy C | this work |
| NMP ⁺ /NMP ⁰ | -0.05 ^a | water/KAc | glassy C | this work |
| Ad ⁺ /Ad | 1.58 ^a | MeCN/0.1 M TEAP | Pt | 38 |
| Qn ⁺ /Qn | 1.97 ^a | MeCN/0.1 M TEAP | Pt | 38 |

^a Standard potential, E° . ^b Half-wave potential, $E_{1/2}$.

TTF-, TTT-, and NMP-TCNQ complexes results in the formation of TCNQ⁰ and oxidation of the donor species, e.g.,

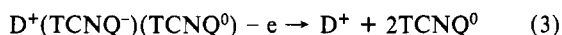


The reduction of TCNQ⁰ observed on scan reversal



then generally accounts for about one-half of the number of coulombs (Q_c) as those consumed during lattice oxidation, Q_a (Table II). The two-electron process in (1) can be ascribed to the fact that lattice oxidation occurs at, or just positive of, the potential for the formation of the donor dication, resulting in the formation of TCNQ⁰ and D²⁺. (Even if the initial reaction did not result in the oxidation of D⁺ to D²⁺, this reaction would still occur, because, as TCNQ⁰ was formed, the uncomplexed D⁺ would be oxidized.) Any uncomplexed TCNQ⁻ would also be oxidized at these applied potentials.

The behavior of the complex 1:2 salts was different than for the 1:1 salts. Lattice oxidation still resulted in the formation of TCNQ⁰.



However, the subsequent reduction of TCNQ⁰ results in a higher number of coulombs consumed compared to lattice oxidation (Table II).



In fact, the reduction peak area was generally equal to or greater than that for the lattice oxidation process.

The electrochemical data can provide information about the free energy of formation of the complex and about the degree of charge transfer between donor and acceptor. There have been many studies on the correlation of polarographic half-wave potentials, $E_{1/2}$, to molecular orbital parameters.³⁹⁻⁴³ A linear correlation between $E_{1/2}$ and the highest occupied molecular orbital (HOMO) (for oxidations) or the lowest unoccupied molecular orbital (LUMO) (for reductions) has been shown for a number of aromatic hydrocarbons, generally with the assumption that the electrode reaction is reversible. The observed electrode potential is related to the free-energy change involved in the reaction. As

Table II. Electrochemical Measurements for Donor-TCNQ Electrodes^a

| electrode | electrolyte | E_{ox}^c | $Q_a^{b,f}$ charge passed | $E_{p,red}^d$ | Q_c^g charge passed |
|---------------------------------|-------------|--------------------|---------------------------------|---------------|-----------------------------|
| TTF-TCNQ | 1 M LiAc | +0.65 | 3.95 | -0.04 | -2.02 |
| TTF-TCNQ | 1 M LiCl | +0.50 | 3.95 | -0.04 | -2.02 |
| TTF-TCNQ | 1 M KBr | +0.49 | 13.8 | +0.03 | -7.87 |
| TTT-TCNQ | 1 M KAc | +0.75 | 0.28 | +0.03 | -0.17 |
| TTT-(TCNQ) ₂ | 1 M KAc | 0.41 | 3.67 | +0.03 | -1.18 |
| NMP-TCNQ | 0.5 M NaF | +0.22 | 2.82 | +0.04 | -1.7 |
| Qn-(TCNQ) ₂ | 1 M KBr | +0.28 ^e | 2.22 | 0.0 | -2.51 |
| | | +0.40 | | | |
| Qn-(TCNQ) ₂ | 1 M KAc | +0.28 ^e | 37.0 | 0.0 | -33.8 |
| | | +0.42 | | | |
| Ad-(TCNQ) ₂ | 1 M KAc | +0.58 | 0.24 | +0.03 | -0.30 |
| Ad-(TCNQ) ₂ | 1 M KAc | +0.58 | 0.74 | +0.03 | -0.75 |
| ferrocenium-(TCNQ) ₂ | 1 M KCl | +0.23 ^e | 0.29 | -0.01 | -0.53 |
| | | +0.43 | | | |
| 2,2-BIP-(TCNQ) ₂ | 1 M KAc | +0.27 ^e | 3.45 | +0.01 | -8.0 |
| | | +0.42 | | | |
| 2,2-BIP-(TCNQ) ₂ | 1 M KBr | +0.27 ^e | 9.2 | +0.01 | -13.0 |
| | | +0.44 | | | |
| 4,4-BIP-(TCNQ) ₂ | 1 M KAc | +0.26 ^e | 7.5 | +0.01 | -12.4 |
| | | +0.50 | | | |

^a Each measurement was made with different electrodes of different areas. ^b The initial process was always an oxidation followed by the reduction process. Charge passed expressed in mC. ^c For initial oxidation scan, taken at a current density of ~25 $\mu\text{A}/\text{cm}^2$ (geometric area), in V vs. SCE. ^d Peak potential for reversal (reduction) scan following lattice oxidation in V vs. SCE. ^e Potential of peak A (see Figures 9 and 10). ^f Initial process. ^g Reversal process.

discussed previously,⁵ molecular complexation results in a shift of the electrode potential. The magnitude of this shift reflects the perturbation of the molecular orbitals due to the complexation and is macroscopically related to the free energy of formation (or the formation constant) of the complex.

If the entropies of formation of the complexes remain constant, the relative stabilities and electrode potentials of the complexes are dependent upon the enthalpy of formation (or free energy of formation) of the complexes.⁴⁴ A linear relationship has been observed between the degree of charge transfer, ρ , and the enthalpies of formation of electron donor-acceptor complexes.⁴⁵ In the case of highly conducting pseudo-one-dimensional organic complexes, the degree of charge transfer, ρ , is a key parameter.⁷ For the TCNQ complexes, ρ can be considered to be the number of electrons per TCNQ molecule. Variation of ρ can occur because of different stoichiometry (i.e., D-TCNQ_n) or because of incomplete charge transfer between the donor and the TCNQ. For the TCNQ stack in these complexes, incomplete charge transfer can be thought of as partial reduction of the TCNQ⁰ to TCNQ⁻. Similarly, ρ on the donor stack must be considered. It has been proposed that ρ is determined by the ionization potential of the donor and the strength of the ionic bonding in the complexes.⁷

There have not been many thermochemical measurements (e.g., heats of formation) made on TCNQ complexes,⁴⁶ other than for TTF, so that a comparison of the results obtained here with thermochemical data cannot be made. From the first redox potentials given in Table I and the potential of the lattice oxidation, the stabilization energy for the TTT-TCNQ and the NMP-TCNQ electrode can be estimated. For TTT-TCNQ, lattice oxidation occurs in 1 M KAc at about +0.75 V vs. SCE and the peak for the formation of TTT⁺Ac⁻ occurs at about +0.24 V vs. SCE. This potential difference yields a stabilization on complexation of 0.51 eV (49.2 kJ/mol). This is a slightly larger stabilization energy than that found previously⁵ for TTF-TCNQ (0.39 eV). For the NMP-TCNQ complex a similar calculation

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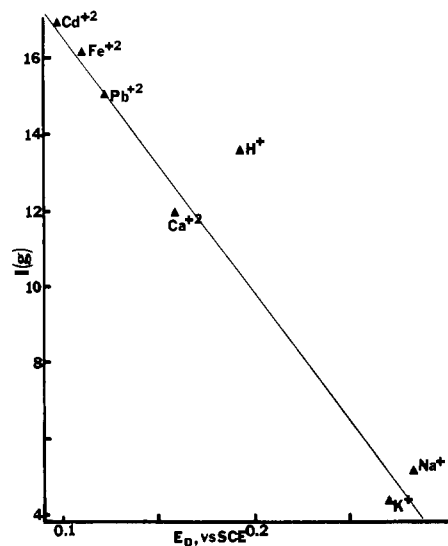


Figure 11. Plot of the anodic peak potential, E_p , for the oxidation of the $M^{n+}TCNQ_n$ layer on a TTF-TCNQ electrode vs. the gas-phase ionization potential, $I(g)$, for M^{n+} .

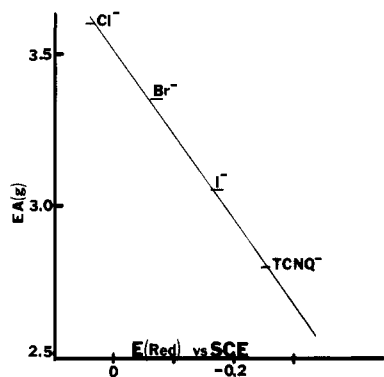


Figure 12. Plot of the cathodic peak potential, $E_{TCNQ-TTFX}^{Red}$, for the reduction of a $TTFX_n$ layer on a TTF-TCNQ electrode vs. gas-phase electron affinity, EA. For TCNQ this is the potential for lattice reduction (EA for TCNQ from ref 47).

yields a stabilization of 0.26 eV (25 kJ/mol).

It is of interest to attempt to correlate the observed potentials for the different processes of these salts with gas-phase ionization potentials [$I(g)$] or electron affinity [$EA(g)$].^{39,40} For example, for the 1:1 TCNQ complexes with TTF and NMP the difference in redox potentials (TTF⁺/TCNQ, 0.32; NMP⁺/NMP, -0.05 V vs. SCE) is in reasonable agreement with the difference in $I(g)$ values (TTF, 6.95;^{47,48} NMP, 6.5 eV⁴⁹).

In our previous study⁵ we reported values of $E_{p,ox}$, the peak potentials for the oxidation $M^{n+}TCNQ_n$ formed on the surface of the TTF-TCNQ electrode by lattice oxidation and then re-

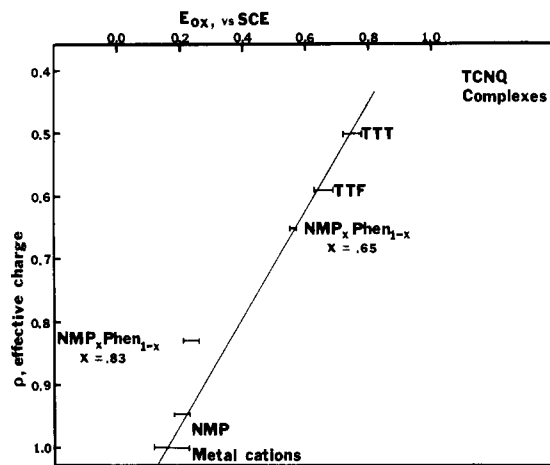


Figure 13. Plot of the potential for lattice oxidation, E_{ox} (vs. SCE), vs. the degree of charge transfer, ρ .

duction in supporting electrolytes with different metal cations, M^{n+} . A plot of $E_{p,ox}$ vs. $I(g)$ for these metal ions⁵⁰ (Figure 11) shows that the correlation is quite good. This probably implies that other factors that influence the $E_{p,ox}$ value (e.g., ion solvation, stabilization energy) cancel out. Similarly, $E_{p,red}$ for the reduction of TTF⁺ X_n^- salts ($X = Cl, Br, I$) formed on the TTF-TCNQ electrode surface by lattice reduction followed by oxidation⁵ show a linear relationship with $EA(g)$ (Figure 12).

The degree of charge transfer, ρ , between the donor molecule and the TCNQ molecules has been a subject of interest. For the series of TCNQ complexes studied here, a linear relationship between the potential of lattice oxidation and ρ was found (Figure 13). In this case, ρ can be thought of as the degree of reduction of TCNQ⁰ to TCNQ⁻.⁷ As ρ decreases from -0.94 (for NMP-TCNQ) to -0.59 (for TTF-TCNQ) the TCNQ moiety becomes more difficult to oxidize (i.e., the potential for oxidation shifts in a positive direction). The 1:2 donor-TCNQ complexes do not follow this correlation, however. For example, Ad-TCNQ₂ ($E_{ox} = +0.58$ V) and Qn-TCNQ₂ ($E_{ox} = +0.28$ V) should have quarter filled bands and $\rho \sim 0.5$. However, the results in Figure 13 suggest that electrochemical measurements might provide a relatively simple method for estimating the degree of charge transfer in these materials. Previously ρ has been determined from susceptibility, optical, and NMR measurements.

Although the results reported here are based upon compressed-disk electrodes, the similarity between the behavior of single-crystal and compressed-disk TTF-TCNQ electrodes suggests that the trends observed accurately reflect the behavior of these complexes. Further studies with compressed-disk and single-crystal electrodes could not only provide information about their chemical behavior but may also lead to new and interesting electrode materials for electrochemical applications.

Acknowledgments. The support of this research by the Robert A. Welch Foundation and the National Science Foundation is gratefully acknowledged. We also appreciate helpful comments and materials from F. Wudl, A. J. Epstein, and J. S. Miller.

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