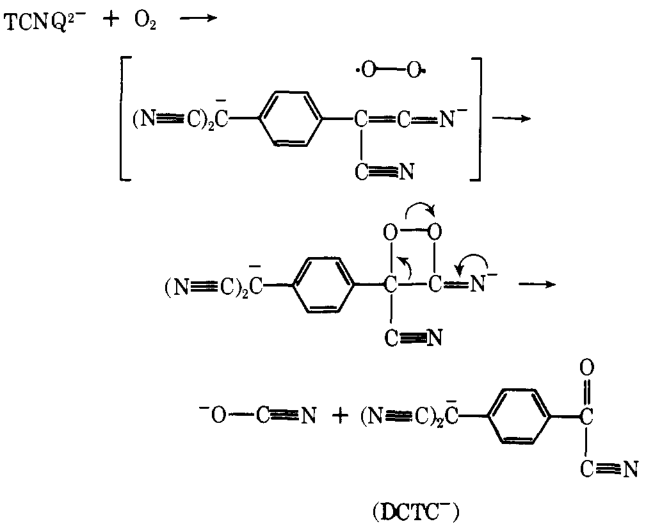
Scheme I



It is undoubtedly possible to work-up the orange reaction mixture, isolate the decay product, and identify it by the conventional spectroscopic methods which have been applied to electrochemical mechanism problems.[18] However, we chose to use this opportunity to evaluate the potential of resonance Raman spectroscopy for electrogenerated product identification. Isolation of the decay product is not necessary in this case since the main components of the electrogeneration medium do not usually produce interfering Raman bands.[12] The resonance Raman spectrum of an O_2 saturated TCNQ^{2-} acetonitrile-0.1 M TBAP solution is shown in Figure 2A. By analogy with the RR scattering spectra of TCNQ and TCNQ$\cdot^-$ [13] the 2214- and 349-cm^{-1} bands of the TCNQ^{2-}-O_2 decay product can be assigned as C≡N stretch and C—C≡N bend, respectively. The 1638-cm^{-1} feature is undoubtedly associated in part with C=C ring stretching but appears too broad to be assigned to only one normal mode. Addition of O_2 to TCNQ^{2-} might result in a C≡N substituted C=O functional group giving rise to an additional Raman band adjacent to the C=C ring stretching mode. Examination of the cyanocarbon chemistry literature for compounds with cyanocarbonyl functionality revealed that the sodium salt of α,α-dicyano-p-toluoylcyanide (NaDCTC) displays infrared absorption bands (conjugated nitrile at 2150 and 2200 cm^{-1}, carbonyl at 1645 cm^{-1}, and conjugated cyanosubstituted double bond at 1590 cm^{-1}) analogous to the observed RR lines of the TCNQ^{2-}-O_2 decay product.[19] The RR scattering spectrum of DCTC$^-$, chemically prepared by the reaction of TCNQ neutral and NO_2^-,[19] is shown in Figure 2B. The exact match between this spectrum of authentic DCTC$^-$ and that of the TCNQ^{2-}-O_2 decay product confirms the decay product's identity as DCTC$^-$. A more detailed examination of the electronic absorption spectrum of chemically prepared DCTC$^-$ reveals two less intense absorption maxima at 330 (ϵ 1.98 × 10^3 M^{-1} cm^{-1}) and 287 nm (ϵ 8.38 × 10^3 M^{-1} cm^{-1}) in addition to the very intense 480-nm band (ϵ 3.92 × 10^4 M^{-1} cm^{-1}). The relative intensities and positions of the 330- and 287-nm absorption bands of DCTC$^-$ also match those previously attributed to TCNQ^{2-}.[15]

A plausible mechanism for the oxygen decay chemistry of electrogenerated TCNQ^{2-} is summarized in Scheme I. TCNQ^{2-} may react with oxygen either via a two-step radical addition or by a $[_\pi 2_s + _\pi 2_a]$ cycloaddition[20] to form a dioxetane intermediate which, in turn, loses a cyanate ion resulting in the formation of the DCTC$^-$ carbanion.

We conclude that the previously reported electronic absorption spectrum of TCNQ^{2-} was spurious and that resonance Raman spectroscopy can be usefully employed for product identification in electrochemical mechanism problems. A more comprehensive study of the formation kinetics and yield of DCTC$^-$ in the reaction of TCNQ^{2-} with oxygen in particular and other small gaseous molecules in general is now in progress.

Acknowledgment. The authors wish to thank Professor F. G. Bordwell for suggesting the DCTC$^-$ formation mechanism presented in Scheme I and Mr. David L. Jeanmaire for assistance in and discussions concerning all phases of this work. The support of this research by the National Science Foundation (MPS74-12573 A01) is gratefully acknowledged.

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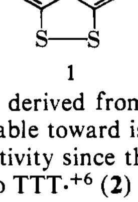
Dehydrotetrathianaphthazarin

Sir:

Our continuing interest in the synthesis of potential organic solid-state conductors[1-4] led us to investigate the preparation of TTN (dehydrotetrathianaphthazarin,[5] naphtho[1,8-cd:4,5-$c'd'$]bis[1,2]dithiole (**1**).



1

Radical cation salts derived from partial oxidation of **1** were expected to be stable toward isolation and give rise to high electronic conductivity since they were expected to be electronically similar to TTT$\cdot^{+6}$ (**2**) and TTF$\cdot^+$ (**3**).

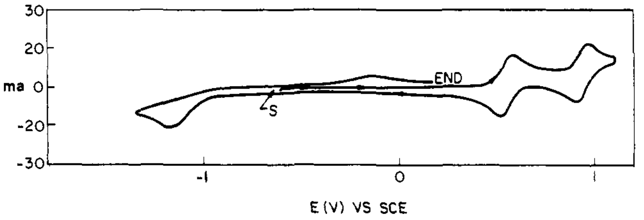
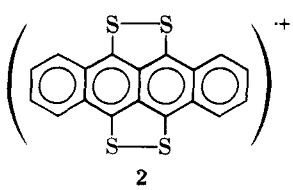
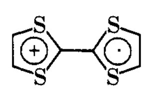


Figure 1. Cyclic voltammogram of TTN (0.01 *M* in CH_3CN): S, start. Scan rate 100 mV/sec.

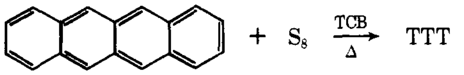


2



3

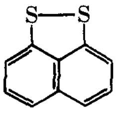
Whereas the preparation of TTT (reaction 1) is quite



(1)

TCB = 1, 2, 4-trichlorobenzene

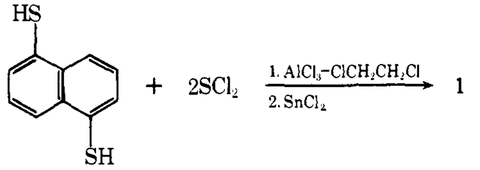
trivial,[7] a similar reaction with naphthalene was reported *not* to afford **1** but to yield **4** in poor yield.[8]. On the other



4

hand, it was reported that octachloronaphthalene reacted with sulfur or sodium disulfide to afford the tetrachloro derivative of **1**.[9] Removal of the chlorine atoms was expected to be difficult (although probably not impossible) because S-S and C-S reductive bond cleavages are considerably easier than aromatic C-Cl reductions.[10] Another possible synthetic route would have been the reaction of naphthalene and sulfur monochloride with a Lewis acid catalyst. Unfortunately, this reaction was reported to afford only polymers[11] (however, vide infra).

We found that **1** was a minor product of reaction 2; the



5

(2)

main products were not characterized. When **5** was treated with 2 equiv of sulfur dichloride (freshly distilled from PCl_5 and stored at −15° over PCl_5) at −5 to 0° followed by 2 equiv of aluminum chloride, **1** could be isolated in 6–10% yield, after reductive work-up, in the form of bronze needles[12] (mp 282–286°, dec, from benzene).

We learned later that reaction of naphthalene with sulfur monochloride in dichloroethane followed by aluminum chloride, afforded **1** in very poor yield (0.01–1% yield as the radical ion detected via ESR spectroscopy of the reaction mixture work-up).

The cyclic voltammogram of **1** (shown in Figure 1), exhibits two reversible oxidation steps ($E_1{}^0 = +0.55$ and $E_2{}^0 = +0.93$ V vs. SCE) in acetonitrile with tetraethylammonium fluoborate as the supporting electrolyte. The peak shapes and separations are consonant with two one-electron processes. Compound **1** also exhibits a reduction (apparently irreversible) step at −1.14 V (peak). The product(s) of this reduction can be reoxidized at −0.06 V (peak).[13]

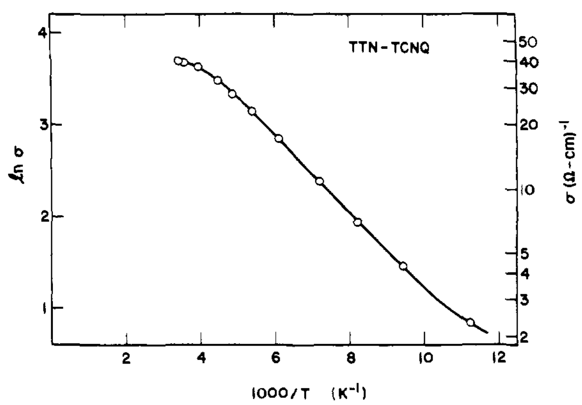


Figure 2. Temperature dependence of the dc conductivity of (TTN)TCNQ.

The ESR spectrum of TTN·+ in formic acid solution is almost superimposable on that of TTF[1] ($g = 2.0094$, $a = 1.52$), a result of the coupling of four equivalent hydrogens with the unpaired spin.

From the above electrochemical results it is easy to conclude that TTN is a much poorer donor than TTF ($E_1{}^0 = +0.36^1$ V, $E_2{}^0 = +0.70^{14}$ V vs. SCE). When a 1:1 mixture of TTN and TCNQ was allowed to react in trichlorobenzene, a mixture of TTN[15] and (TTN)TCNQ was isolated in ca. 90% yield and in a ratio of 1:3. The latter compound was isolated as black needles and the former as red (by transmission) plates. These had to be separated mechanically since their solubility properties were similar in several solvents. In acetonitrile, the complex reverts to TTN (which precipitates) and TCNQ (which remains in solution).

The results of measurements performed by the four probe technique[4] on a single crystal (ca. 1 × 0.03 × 0.03 mm) of (TTN)TCNQ are shown in Figure 2. As can be seen (Figure 2), the conductivity of one single crystal[16] of (TTN)TCNQ between room temperature and ca. 200 K is 40 Ω^{-1} cm^{-1}, considerably higher than (TTT)TCNQ (1 Ω^{-1} cm^{-1})[17] and the same as the microwave conductivity of most $TTT(TCNQ)_2$ crystals.[16,18]

We are actively pursuing the preparation of suitably substituted TTN (and its selenium analogue) and the use of TTN itself in the preparation of organic-inorganic conductors.

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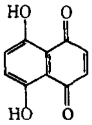

i

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(13) There is no need to discuss the two oxidation waves (0.55 (peak) and 0.93 V (peak), as suggested by a referee) because they are clean, fully reversible redox steps much like those found in simple inorganic systems (e.g., $Cu \rightleftarrows Cu^{I} \rightleftarrows Cu^{II}$, etc.). They are not encumbered by coproportionation or disproportionation problems since the radical cation is *indefinitely* stable in solution and can be *isolated.* However, the reduction wave (−1.14 V, peak) followed by reoxidation to TTN at −0.06 V (peak) deserves some explanation which should be deferred to the full paper on this subject.
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On the Sensitive Probe for Double Layer Structure. Potential Dependent Competitive Cyanation and Methoxylation of 1,4-Dimethoxybenzene

Sir:

A recent paper by Weinberg et al.,[1] which deals with a competitive anodic cyanation and methoxylation, contains serious errors which cast considerable doubt upon their conclusions. They calculated the concentration of cyanide and methoxide ions using Ritchie's $K_b \simeq 10^{-3}$ M for cyanide,[2] however, overlooked the fact that the equilibrium constant did not contain the solvent term. Thus a 0.5 M NaCN-CH_3OH solution will actually contain approximately 0.48 M cyanide and 0.02 M methoxide ions. This shows that, if their assumptions are correct, the ratio of (CN^-/CH_3O^-) in the bulk of solution becomes greater than that at the electrode at the 1.3 V or less potential region (see Table II in ref 1). This is a queer result in view of both strong chemisorption of cyanide ion on platinum[3,4] and the independence of the product distribution on potential.[5] Even at as low a potential as 0.4 V, cyanation occurs efficiently.[6] In case II, the correct numerals cannot be used, since the value of **3y** would be greater than that of **3.**[7]

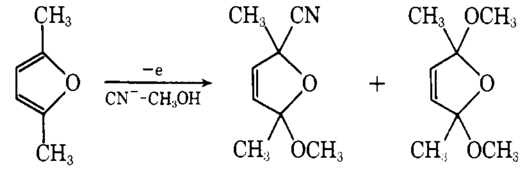
Previously we reported the competitive cyanation and methoxylation of 2,5-dimethylfuran.[5] A 2:1 isomeric mixture of *cis*- and *trans*-2-cyano-5-methoxy-2,5-dimethyldihydrofurans was formed together with small amounts of *cis*- and *trans*-2,5-dimethoxy-2,5-dimethyldihydrofurans. There was no variation in product distribution over a significant region of concentration (0.1-0.8 M). The product distribution was also unaltered with anode potential. These observations clearly show that nucleophiles are strongly adsorbed on the anode and do not vary markedly with the bulk concentration or potential. The analogous situation should also be maintained in the case of 1,4-DMB at the same material electrode. Thus the origin of apparent potential dependency of the current efficiencies of anisocyanide and the quinone diketal must be sought for elsewhere. One explanation may be that the cation radical of 1,4-DMB is not adsorbed as strongly as is that of 2,5-dimethylfuran, diffuses into the bulk solution which contains a greater relative concentration of methoxide ion, and consequently produces a greater part of the quinone diketal with the decreasing in sodium cyanide or with the lowering in anode potential. Table I shows the relation between the ratio of cyanide and methoxide ions at equilibrium and an initial concentration of sodium cyanide. It is apparent from the table that the relative concentration of methoxide ion increases with the decreasing of the initial concentration of sodium cyanide.

Table I. Relative Concentration of Cyanide and Methoxide Ions at Equilibrium in Methanol[a]

[NaCN], M	(CN^-/CH_3O^-)
0.1	9.5
0.5	21.7
1.6[b]	39.0

[a] $K_b \simeq 10^{-3}$ M, ref 2. [b] Saturated solution.

Scheme I



There is a question of whether nucleophilic reactions occur with cyanide and methoxide *on* the electrode or in the region of solution next to the electrode (i.e., the double layer) extending out from the electrode about 10 Å.[1] If nucleophilic attack occurs in a heterogeneous environment (i.e., on the electrode), reaction will proceed stereospecifically. The cyanomethoxylation products of 2,5-dimethylfuran were, however, equilibrium mixtures of the cis and trans isomers.[5] In addition, the addition of substrate such as cyclohexene or toluene, which has a high oxidation potential, results in a remarkable decreasing of the current in the region 1.4–1.8 V. Substrate is strongly adsorbed on the anode to expel cyanide and methoxide ions. Hence we support their proposal, i.e., reaction of nucleophile with anodically produced cationic species occurs in the double layer.

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