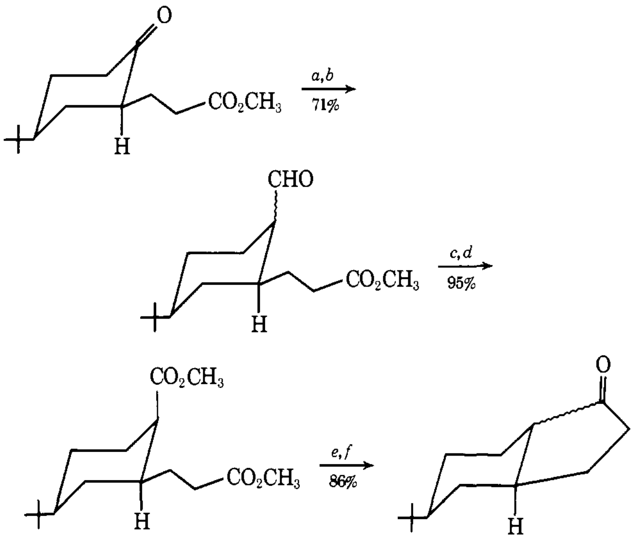
Scheme I



^{a}Ph$_3$$^+PCH_2OCH_3Cl^-$, n-C$_4H_9Li, Et_2$O, reflux. ^{b}HClO$_4$, H$_2O, CH_2Cl_2$, reflux. ^{c}CrO$_3$, (CH$_3$)$_2CO, H_2O, H_2SO_4$, room temperature. ^{d}CH$_2$N$_2$, Et$_2$O, room temperature. ^{e}NaH, CH$_3$OH, Et$_2$O, reflux. ^{f}NaCl, H$_2$O, DMSO, 160°.

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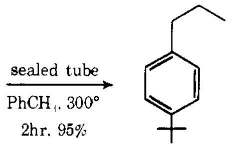

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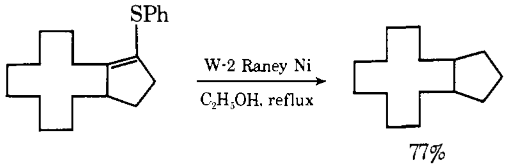
radical and will be discussed subsequently.

Other advantages of this new approach in addition to those mentioned in the introduction include the inexpensive cost and large scale availability of cyclopropylphenyl sulfide and the ease of handling the intermediates along the path. It furthermore expands the synthetic flexibility since the intermediate enol thioethers can in principle be desulfurized[10] to yield regiospecifically generated cyclopentenes, hydrolyzed to give regiospecifically generated α-bromo ketones[11] and therefore regiospecifically generated cyclopentenones or hydrogenated (eq 2) to the cyclopentane.



(2)

Acknowledgment. We wish to thank the National Institutes of Health and the National Science Foundation for their generous support of our programs.

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(4) (a) E. M. Burgess, H. R. Penton, and E. A. Taylor, *J. Org. Chem.*, **38**, 26 (1973). (b) Choice of the dehydrating method is important since dehydration accompanied with rearrangement to a cyclobutene thioether[3b] can become the major, if not exclusive, course. In one case, the use of a xanthate pyrolysis at 150° in HMPA was the preferred method.

(5) (a) Conditioning of the column consisted of treating the preheated (250°) column with *O,N*-bistrimethylsilylacetamide followed by hexane. (b) Conditioning of the sealed tubes involved drying under N$_2$ at 120° for 12 hr and washing with *O,N*-bistrimethylsilylacetamide followed by benzene. Pyrolyses in sealed tubes were performed in vacuo at ~0.1 mm.

(6) All new compounds had spectral properties and analytical data in complete accord with the assigned structure.

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Resonance Raman Spectroelectrochemistry. IV. The Oxygen Decay Chemistry of the Tetracyanoquinodimethane Dianion

Sir:

Currently there is a high level of interest in the charge-transfer salts of tetracyanoquinodimethane (TCNQ) with certain organic donor molecules such as tetrathiofulvalene (TTF) which display large electrical conductivities and "metallic" properties over a wide temperature range.[1] A variety of molecular orbital calculations have been carried out on TCNQ, TCNQ$\cdot^-$, TCNQ^{2-}, (TCNQ)$_2$, (TCNQ$\cdot^-$)$_2$, poly(TCNQ), poly(TCNQ$\cdot^-$), and poly(TCNQ^{2-}) as well as the corresponding TTF moieties in an effort to develop a more detailed picture of the electronic structure of these materials.[2-5] In order to evaluate and provide experimental support for these increasingly more sophisticated calculations, it is necessary to obtain reliable measurements of both ground and excited state properties of monomeric TCNQ, TTF, and their ions as well as the corresponding dimers. Electronic absorption spectroscopy[6,7] and electron spin resonance spectroscopy[8] have been widely used to provide such data. Recently vibrational spectroscopy has been recognized as an important tool for the characterization of charge-transfer solids.[9-11]

In a recent paper we reported the successful interfacing of electrochemical species generation with vibrational spectroscopic observation based on the resonance Raman (RR) effect to produce the hybrid technique of resonance Raman spectroelectrochemistry (RRSE).[12] Using tetracyanoethylene (TCNE) as a test system, we demonstrated that RRSE was an effective means of measuring the ground state vibrational frequencies of the totally symmetric bond stretching modes of TCNE$\cdot^-$ in a minimally perturbing environment. Comparison of the TCNE$\cdot^-$ vibrational frequencies measured by RR scattering spectroscopy with the corresponding TCNE vibrational frequencies measured by normal Raman (NR) spectroscopy yielded the electron transfer induced vibrational shifts which were then compared with the appro-

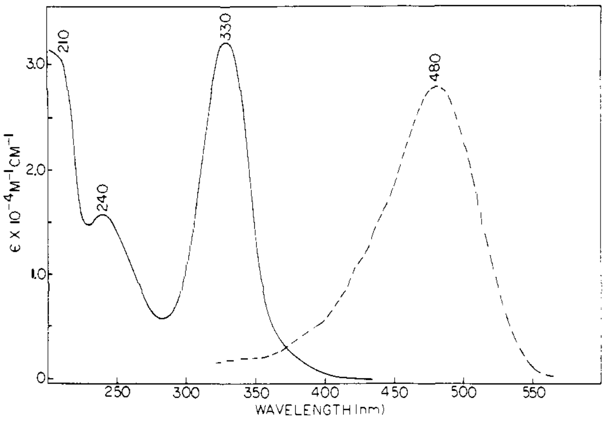


Figure 1. Electronic absorption spectra of 2.55 × 10^{-4} *M* TCNQ in *M* TBAP-acetonitrile solution following exhaustive $2e^-$ reduction at −0.70 V vs. SCE: solid line, $TCNQ^{2-}$ absorption spectrum obtained by rigorous exclusion of O_2 from the electrogeneration environment; dotted line, absorption spectrum obtained by electrogenerating $TCNQ^{2-}$ in the presence of O_2 or by bubbling O_2 through the solution which gave the solid line spectrum. The extinction coefficient scale is quantitatively accurate for the $TCNQ^{2-}$ (solid line) spectrum only.

priate π-bond order changes resulting from a molecular orbital calculation. This initial study has now been extended to include both the RR scattering spectroscopy of electrogenerated $TCNQ\cdot^-$ accompanying excitation of its lowest $^2B_{1u}$ excited state $(^2B_{1u}{}^{(1)})$[13] and the tunable dye laser RR excitation spectroscopy of the $^2B_{1u}{}^{(1)}$ state for the ν_2, ν_4, ν_5, and ν_9 totally symmetric modes.

In addition to its importance in charge-transfer solids, one of the reasons TCNQ was chosen as an excellent candidate for RRSE examination was a report by Jonkman and Kommandeur[15] that the electronic absorption spectrum of electrogenerated $TCNQ^{2-}$ had an absorption maximum of ca. 2.6 eV (477 nm). On this basis it was considered feasible to obtain the RR scattering spectrum of $TCNQ^{2-}$ using the 4880 Å Ar^+ laser line as the excitation source and thereby measure the vibrational frequency shifts for the observable totally symmetric modes which accompany the transformation $TCNQ\cdot^- + e^- \rightarrow TCNQ^{2-}$. This communication describes our attempted RRSE study of electrogenerated $TCNQ^{2-}$.

The controlled potential electrolysis electrogeneration mode was used for all the RRSE experiments in this study. The apparatus and procedures for carrying out this type of RRSE experiment as well as the method of TCNQ purification have been previously described.[12-14]

Cyclic voltammetric examination of TCNQ in O_2 free (N_2 sparging technique) acetonitrile containing 0.1 *M* tetrabutylammonium perchlorate (TBAP) demonstrates that the one-electron reductions to form $TCNQ\cdot^-$ and $TCNQ^{2-}$ are both electrochemically and chemically reversible on the 0.2-2.0-second time scale.[13]

$$TCNQ + e^- \rightarrow TCNQ\cdot^- \quad E_1{}^0 \approx E_{1/2,1} = +0.20 \text{ V vs. SCE} \quad (1)$$

$$TCNQ\cdot^- + e^- \rightarrow TCNQ^{2-} \quad E_2{}^0 \approx E_{1/2,2} = -0.33 \text{ V vs. SCE} \quad (2)$$

This is in general agreement with earlier dc polarographic results.[16,17] The long term chemical stability of $TCNQ\cdot^-$ electrogenerated in this medium was shown to be in excess of 3 hr by controlled potential reversal coulometry.[13] An identical chemical stability test has now been performed for $TCNQ^{2-}$. Stepping the applied potential from an initial value of +0.60 V vs. SCE, where TCNQ is electroinactive, to any value in the range −0.50 to −0.80 V vs. SCE, where electrode reactions (1) and (2) proceed at a mass transport (convective stirring) limited rate, the number of Faradays consumed per mole of TCNQ, n_{app}, was 1.95 ∓ 0.05. On returning the applied potential to its initial value, the ratio of charge consumed in the reverse electrolysis to that consumed in the forward electrolysis, Q_r/Q_f, was found to be 0.95 ∓ 0.07. Both n_{app} and Q_r/Q_f were independent of bulk TCNQ concentration over the range 0.1-2.0 m*M*. The forward electrolysis period was 20 min. Thus it can be concluded that $TCNQ^{2-}$ electrogenerated under these conditions is chemically stable for at least 40 min (forward plus reverse generation periods).

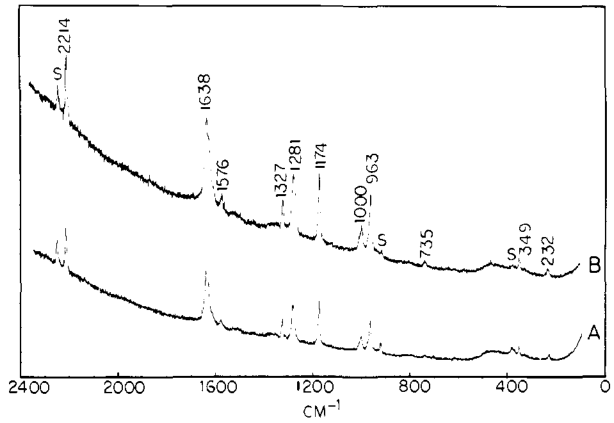
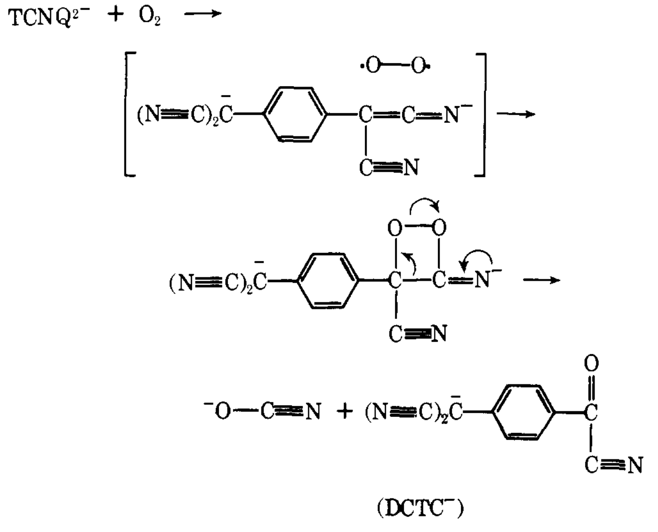


Figure 2. Resonance Raman spectra of: (A) electrogenerated $TCNQ^{2-}$ saturated with O_2 ($[TCNQ^{2-}] = 1.42 \times 10^{-3}$ *M*, laser power at 4579 Å = 80 mW, band-pass = 2.3 cm^{-1}) (B) authentic $DCTC^-$ in CH_3CN:H_2O (10:1); ($[DCTC^-] = 1.43 \times 10^{-3}$ *M*, laser power. at 4579 Å = 30 mW, band-pass = 2.3 cm^{-1}) $TCNQ^{2-}$ was electrogenerated by controlled potential coulometry at −0.70 V vs. SCE in 0.1 *M* TBAP-CH_3CN. All spectra were scanned at ca. 50 cm^{-1} min^{-1} using a 1.00-sec counting interval. Plasma lines were removed with a 4579 Å. interference filter.

The electronic absorption spectrum of 2.55 × 10^{-4} *M* $TCNQ^{2-}$ electrogenerated under O_2 free conditions at −0.70 V vs. SCE and recorded less than 5 min after completion of the forward electrolysis is shown in Figure 1 (solid line). This spectrum, which has absorption maxima at 3.75 (330 nm), 5.16 (240 nm), and 5.90 eV (210 nm), has no visible absorption band at 2.6 eV (477 nm) contrary to the report of Jonkman and Kommandeur.[15] If, however, trace or larger amounts of O_2 are admitted to the electrolysis cell after electrogeneration to form a colorless $TCNQ^{2-}$ solution, the solution immediately turns orange. The absorption spectrum of the same electrogenerated $TCNQ^{2-}$ solution following saturation with O_2 is shown as a dotted line in Figure 1. The 2.6 eV (477 nm) absorption maximum of this $TCNQ^{2-}$-O_2 decay product matches the absorption maximum of the visible band reported by Jonkman and Kommandeur. Evidently the previously reported $TCNQ^{2-}$ absorption spectrum was contaminated by some of this decay product spectrum and the longest wavelength absorption band of $TCNQ^{2-}$ is actually 330 nm. This unfortunately precludes the RRSE examination of $TCNQ^{2-}$ until we obtain the necessary apparatus to enable such experiments to be carried out using the 3511 and 3638 Å uv Ar^+ laser lines for excitation. It should be noted that Bieber and Andre[2] were suspicious of the poor agreement between experimental and SCF MO calculated electronic transition energies for $TCNQ^{2-}$ in view of the relatively good agreement between the corresponding comparisons for TCNQ and $TCNQ\cdot^-$. Since an O_2 decay product free absorption spectrum for $TCNQ^{2-}$ is now at hand, a better theory-experiment comparison should be possible.

We now turn to the question of the identity of the $TCNQ^{2-}$-O_2 decay product and its formation mechanism.

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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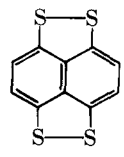
Dehydrotetrathianaphthazarin

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**).