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An Investigation of the Factors that Influence the Decomposition of 7,7′,8,8′-Tetracyanoquinodimethane (TCNQ) and Its Salts to, and Structural Characterization of, the α,α-Dicyano-*p*-toluoylcyanide Anion

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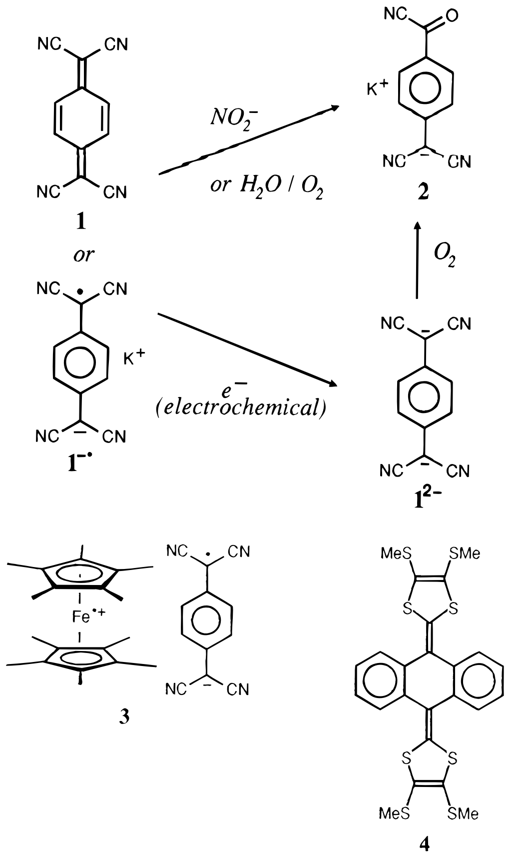
The kinetics of formation of α,α-dicyano-*p*-toluoylcyanide anion (DCTC$^-$) by reaction of TCNQ^0 and its radical anion salts with nitrite ion have been investigated spectroscopically; the reaction of TCNQ^0 with excess nitrite is first order, whereas oxidation of TCNQ$^{\bullet-}$ appears to proceed via TCNQ^0 as an intermediate. The first X-ray structural study of a simple DCTC$^-$ salt, K$^+$[2.2.2] DCTC$^-$, is also reported.

Introduction

Decomposition of 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) **1** and its radical anion and dianion salts $\mathbf{1}^{\bullet-}$ and $\mathbf{1}^{2-}$, respectively, to the α,α-dicyano-*p*-toluoylcyanide anion (DCTC$^-$) **2** (Scheme 1) represents a potential limitation for the exploitation of these electronically interesting materials. This process was first reported by Hertler and co-workers[1] when they isolated an orange-red DCTC$^-$ salt from reaction of TCNQ^0 with nitrite ion. The same outcome was subsequently observed[2] from aerial oxidation of TCNQ^{2-} (generated electrochemically from **1**), and an X-ray structural study by Miller and co-workers[3] of the metamagnetic phase of decamethylferricenium TCNQ$^{\bullet-}$ **3** revealed contamination by DCTC$^-$ arising from solid-state reaction of monomeric TCNQ$^{\bullet-}$ anions with dioxygen (the paramagnetic phase of this material that contains (TCNQ$^{\bullet-}$)$_2$ dimers being air stable).

A similar problem has been encountered on crystallization of the TCNQ salt of the TTF (TTF = tetrathiafulvalene) analogue **4**, which can be readily oxidized to a dication facilitating formation of TCNQ^{2-}.[4] However, although several mixed TCNQ/DCTC salts have been characterized and attempts have been made to investigate the mechanism of this decomposition process,[5] no detailed X-ray structural study of a pure sample of a DCTC$^-$ salt has as yet been described, a situation that we now rectify.

Scheme 1. Decomposition of TCNQ 1 and its salts to DCTC− 2.



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Experimental Section

Preparation of Potassium 7,7′,8,8′-Tetracyano-*p*-quinodimethanide (KTCNQ). KTCNQ was prepared in the usual manner,[6] by reaction of a solution of $TCNQ^0$ (5 mmol) in dry acetonitrile (50 mL) with KI (7.5 mmol), as dark purple crystals (0.93 g, 77%), mp > 300 °C (lit.[6] > 300 °C decomp.); IR ν_{max} (cm^{-1}, Nujol): 2193, 2180 and 2164 (C≡N), 1576 (C=C(CN)$_2$ stretch), 1506 (aromatic C−C), 1364 (C−H), 1181 (C−CN), 985 (C−C ring stretch), 822 (1,4 disub. ring), 720 (C−H). Found: C, 59.27; H, 1.69; N, 23.02. $C_{12}H_4N_4K$ requires: C, 59.25; H, 1.66; N, 23.03%.

Preparation of Potassium α,α-Dicyano-*p*-toluoyl cyanide (KDCTC), 2. *(i) By Reaction of $TCNQ^0$ with KNO_2.* KDCTC **2** was prepared[1] from $TCNQ^0$ by reaction of a solution of KNO_2 (1.29 mmol) in water (4 mL) with a warm solution of TCNQ (0.74 mmol) in acetone (50 mL). The resulting dark red solution was evaporated to dryness in vacuo, and the residual black solid was crystallized from acetone and dichloromethane as a dark red powder (0.10 g, 58%); IR ν_{max} (cm^{-1}, powder): 2198 and 2154 (s, C≡N), 1627 (w sh), 1568 (s, C=C(CN)$_2$), 1506 (s, aromatic C=C), 1360 (s), 1184 (s, C−CN + C−C ring), 833 (C=C ring, stretch), 744 (1,4 disub. ring); ν_{max} (cm^{-1}, acetone) 2183, 2152 and 2134 (s, C≡N), 1637 (w, C=O), 1574 (s, C=C(CN)$_2$), 1507 (s, aromatic C=C), 1179 (s C−CN + C−C ring); UV λ_{max} (ϵ_{max}) (nm (M^{-1}), H_2O): 468 (31600), 335 (2700), 274 (2400), 222 (9200); NMR δ (^1H, ppm, d_6-acetone) 6.90 (2H, d, J = 8 Hz), 7.65 (2H, d, J = 8 Hz); δ (^{13}C, ppm, d_6-acetone) 161.2 (C=O), 153.4, 130.7 (aromatic CH), 129.4, 121.7 (aromatic C), 120.1, 117.1, 113.8 (C≡N), 113.6 (C≡N), 113.1 (C≡N), 40.5 (C^-); δ (^{13}C, ppm, CP MAS): 160.9, 155.1, 135.9, 129.8, 122.7, 120.6, 118.9, 117.4, 114.8, 113.4, 45.3. Further purification of this compound (e.g., by recrystallization) was hampered by its instability, a problem previously encountered[1] with other alkali metal $DCTC^-$ salts.

(ii) By Reaction of KTCNQ with KNO_2. KDCTC was prepared from KTCNQ in a manner similar to that just described. A solution of KNO_2 (1.65 mmol) in water (5 mL) was added to a solution of KTCNQ (0.99 mmol) in acetone (50 mL). The resulting dark orange-red solution was evaporated to dryness in vacuo, to give a black solid that was purified as already described affording a dark red powder (0.10 g, 44%). This power gave spectra identical with those described in (i).

Preparation of (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)-potassium 7,7′,8,8′-tetracyano-*p*-quinodimethanide (K[2.2.2]TCNQ), 5. Slow cooling of a hot solution of KTCNQ (2.5 mmol) and [2.2.2]-cryptand (2.5 mmol) in CH_3CN (10 mL) gave K[2.2.2]TCNQ as dark blue microcrystals (0.97 g, 63%); mp 195−200 °C decomp. (lit.[7,8] 137 °C); IR ν_{max} (cm^{-1}, KBr disk): 2963(w) and 2877(w) (C−H), 2180(s) and 2153(s) (C≡N), 1589(m) (C=C(CN)$_2$), 1508(s) (aromatic C=C), 1363(s) (C−H), 1137(s) (C−CN and C−C(aromatic)), 1095, 1023, 918. Found: C, 58.13; H, 6.51; N, 13.50. $C_{30}H_{40}N_6O_6K$ requires C, 58.14; H, 6.50; N, 13.56%.

Preparation and X-ray Structural Characterization of (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)-potassium α,α-dicyano-*p*-toluoyl cyanide (K^+[2.2.2] $DCTC^-$), 6. Although attempts to grow X-ray quality single crystals of K[2.2.2]TCNQ **5** from acetonitrile by slow evaporation failed to produce any satisfactory samples of that complex, several single purple-black crystals were isolated that proved to be samples of the corresponding DCTC salt **6**. One of the latter, measuring ~0.13 × 0.12 × 0.08 mm, was used for the data collection. Data reduction was performed using RC85,[9] and the structure was solved by direct methods (SHELXS-86[10]) and difference Fourier techniques refinement using the CRYSTALS suite of programs.[11] Corrections for anomalous scattering and extinction were also applied as was a two-term Chebyshev polynomial weighting scheme.[12] The last cycle of least squares refinement converged with R = 4.67% (R_w = 5.74%). Full details of the data collection and refinement are summarized in the Supporting Information, together with additional figures and tables of atomic coordinates, selected bond angles, bond lengths, interatomic distances, and thermal parameters.

Kinetic Experiments. The kinetics of the oxidation of TCNQ were followed by monitoring the ultraviolet−visible (UV−vis) spectrum of the reacting solution. KNO_2 (1.5 mL, 10 mM in water) was added to a solution of KTCNQ (1.5 mL, 0.1 mM in acetone) in a cuvette at 20 °C. The UV−vis spectrum of the resulting mixture was recorded over the range 370−800 nm, and changes of absorbance with time at characteristic wavelengths were monitored; [$TCNQ^{\bullet -}$] was determined at 725 nm (where $\epsilon_{TCNQ^{\bullet -}} = 14\,800\ M^{-1}$) and [$DCTC^-$] was determined at 469 nm (where $\epsilon_{DCTC} = 29\,800\ M^{-1}$). Molar extinction coefficients in acetone/water (1:1) solutions were determined for $TCNQ^0$, KTCNQ, and KDCTC. The absorption band for $TCNQ^0$ overlapped those of other species. However, from a knowledge of the concentration of $TCNQ^{\bullet -}$ and molar extinction coefficients at 392 nm for $TCNQ^0$ ($\epsilon_{TCNQ^\circ} = 50\,400\ M^{-1}$) and $TCNQ^{\bullet -}$ ($\epsilon_{TCNQ^{\bullet -}} = 20\,000\ M^{-1}$), obtained from measurements of the spectra of solutions of pure compounds of known concentrations, it was possible to calculate the concentration of $TCNQ^0$ at this wavelength.[13]

The uncertainty in measurement of concentrations and extinction coefficients arises from the uncertainty in determining an absorbance, which for all measurements was taken as 0.01 absorbance units. If it is assumed that this uncertainty is a rectangular distribution, the standard uncertainty in the absorbance $u_A = 0.01/3$ and the standard uncertainties for each of the concentrations may be determined in the usual way.[14]

Results and Discussion

Following well-established procedures,[15] rapid crystallization of KTCNQ from acetonitrile in the presence of [2.2.2]-cryptand gave a pure black microcrystalline powder sample of the [2.2.2]-cryptate **5** for which satisfactory spectroscopic and analytical data have been obtained.[7,8] However, while attempts to grow larger single crystals of **3** have so far proved unsuccessful; in the course of this work good-quality, purple-black single crystals were isolated that have been shown by X-ray structural analysis to be the [2.2.2]-cryptate of K^+ $DCTC^-$, **6**, as its acetonitrile solvate.

The asymmetric unit of **6** is shown in Figure 1. There is no close contact between neighboring $DCTC^-$ moieties nor is there any evidence for direct interaction between the anion and the cryptand-encapsulated cation, the closest contact (to N_{14}) being 4.389(3) Å. The cryptand itself adopts the typical *endo*−*endo* type configuration,[16]

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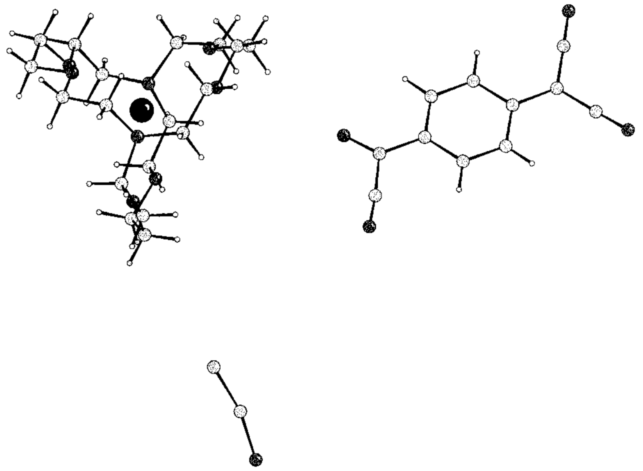
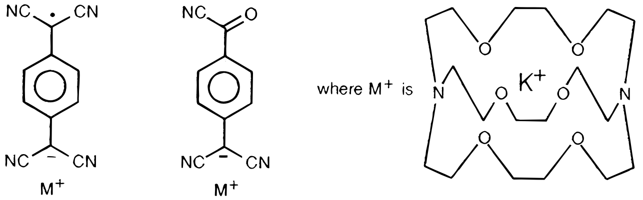


Figure 1. The asymmetric unit of K[2.2.2]DCTC·CH_3CN **6** showing the crystallographic numbering scheme employed (hydrogen atoms are excluded).



5 **6**

with the potassium ion lying centrally within the cage and average K^+—N and K^+—O distances of 3.0 and 2.8 Å, respectively. The salt **6** adopts a packing arrangement in which sheets of [2.2.2]K^+ units are separated by channels containing the isolated $DCTC^-$ monomers. The additional solvent molecules are disordered and are located in the same sheets as the [2.2.2]K^+ units.

The geometry of the $DCTC^-$ anion is very similar to that found in the mixed TCNQ/DCTC salt of **4**.[4] The cyano group bond lengths are slightly shortened relative to those found in $TCNQ^0$, in a manner similar to that observed when the latter is reduced to its radical anion.[17] The carbonyl group bond length in the $DCTC^-$ anion in the K[2.2.2]-cryptate salt **6** has a value that is comparable with those reported for benzoquinones and diaryl ketones, but slightly shorter than that observed in carboxylate ions.[18]

Infrared Studies of KDCTC 2. Infrared spectra of KDCTC **2** show a surprisingly weak carbonyl absorption at ~1638 cm^{-1} and strong cyanide absorptions in the region 2135−2185 cm^{-1}. The value of $\nu_{C=O}$ reported here is similar to those previously observed for the carbonyl stretching frequencies in other $DCTC^-$ salts (1645 cm^{-1} in Me_4N DCTC,[1] 1650 cm^{-1} in NaDCTC[1] and 1624 cm^{-1} in $Me_{10}Fc$ DCTC **5**[3]). In an IR/Raman study of the behavior of M^+ $DCTC^-$ salts ($M^+ = Cu^+$, Ag^+ and K^+) Mazur and co-workers[19] have observed comparable changes in the position of the carbonyl vibration for spectra obtained from such compounds as KCl disks, polycrystalline samples or solutions in CH_3CN. They conclude that environmental effects play only a small role in determining the internal vibrational frequencies of the $DCTC^-$ ion. However, in the present study the weak carbonyl absorption could not be resolved in ATR spectra recorded from solid samples of **2** (as a microcrystalline powder or in a Nujol mull) or in transmission spectra obtained from solutions of **2** in ethanol. To investigate this behavior further, Raman spectra were obtained of each of these samples. These revealed a carbonyl peak at 1624 cm^{-1} (solid samples) and 1626 cm^{-1} (ethanol solution) which, in the infrared spectra obtained under these conditions, is masked by the very intense and rather broad band at ca. 1580 cm^{-1}.

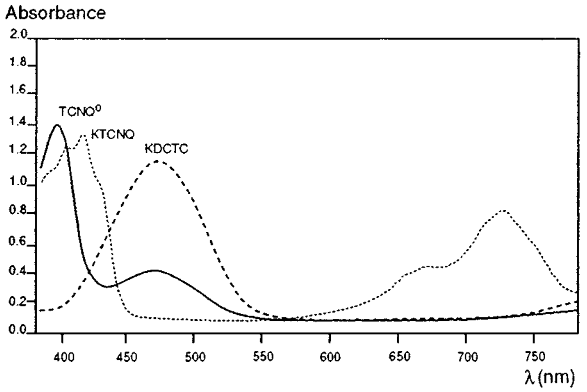


Figure 2. Overlay of the visible spectra of 10^{-4} M solutions of $K^+TCNQ^{\bullet-}$(- - -), $TCNQ^0$ (—), and K^+DCTC^- (− − −) in aqueous ethanol.

The position and low infrared intensity of the C=O stretching frequency in the $DCTC^-$ ion suggests some enolate character **7** in this species, as reflected by the somewhat elongated C=O bond observed in the solid-state structure of **6**.

UV−Visible Spectroscopic Studies of K^+DCTC^- 2. Solutions of K^+DCTC^- **2** in water are unstable. The orange solution that is initially formed has λ_{max} (ϵ_{max}) 468 (20 000), 334 (2 700), 274 (2 400), 222 (9 200) nm, but this color fades over 24 h to λ_{max} 334 and 224 nm. An EtOH solution, which also has λ_{max} 468 nm, fades more slowly. The UV−vis spectrum of **2** is compared with those of $TCNQ^0$ and KTCNQ in Figure 2.

NMR Spectroscopic Studies of K^+DCTC^- 2. The ^1H NMR spectrum of K^+DCTC^- **2** in d_6-acetone is almost identical with that previously reported for *N*-benzylpyridinium $DCTC^-$.[5] A ^{13}C NMR spectrum recorded under the same conditions shows a carbonyl resonance at δ 163 ppm. The solid-state ^{13}C CPMAS NMR spectrum of a microcrystalline sample of KDCTC **2** is almost identical with that observed for solutions of **2** in d_6-acetone.

Kinetic Analysis of the Nitrite-Induced Decomposition of $TCNQ^{\bullet-}$. In a study of the air-induced decomposition of $TCNQ^{\bullet-}$, Mizoguchi and co-workers[20] determined that formation of the product, $DCTC^-$, occurred via $TCNQ^0$ as an intermediate. Their suggested mechanism was:

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$$2\ \mathrm{TCNQ}^{\bullet-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{TCNQ}^0 + \mathrm{TCNQ}^{2-} \tag{1}$$

$$\mathrm{TCNQ}^0 \xrightarrow[k_2]{[\mathrm{O}]} \mathrm{DCTC}^- \tag{2}$$

Having used the nitrite-induced decomposition of $\mathrm{TCNQ}^{\bullet-}$ to prepare salts of KDCTC **2**, we decided to investigate this process further. A kinetic study over a limited range of concentrations appeared to support a second-order reaction (a plot of the rate of change of $[\mathrm{TCNQ}^{\bullet-}]$ varied as $[\mathrm{TCNQ}^{\bullet-}]^{1.9}$). However, inspection of the concentrations of reactant $\mathrm{TCNQ}^{\bullet-}$, product $\{\mathrm{DCTC}^-\}$, and intermediate $\{\mathrm{TCNQ}^0\}$ (Figure 3) reveal a long induction time that cannot be explained by a simple model of the form implied by eqs 1 and 2.

These observations suggest that the nitrite-induced decomposition of $\mathrm{TCNQ}^{\bullet-}$ involves an autocatalytic pathway in which TCNQ^0 promotes the oxidation of $\mathrm{TCNQ}^{\bullet-}$ to TCNQ^0 (eq 3). Our results (Figure 4) also support the view that the subsequent conversion of TCNQ^0 to DCTC^- in the presence of nitrite proceeds by a pseudo-first-order pathway as was proposed by Mizoguchi (eq 4).[20]

$$\mathrm{TCNQ}^0 + \mathrm{TCNQ}^{\bullet-} \xrightarrow[k_3]{\mathrm{NO_2}^-} 2\ \mathrm{TCNQ}^0 \tag{3}$$

$$\mathrm{TCNQ}^0 \xrightarrow[k_4]{\mathrm{NO_2}^-} \mathrm{DCTC}^- \tag{4}$$

Although it may be assumed that the initial concentration of TCNQ^0 present will result from the disproportionation of $\mathrm{TCNQ}^{\bullet-}$, as proposed by Mizoguchi[20] (eq 1), once the reaction is underway, the predominant source of TCNQ^0 is likely to be via eq 3. If this is true, in the presence of excess nitrite, the rate equations for the proposed mechanism will be:

$$\frac{\mathrm{d}[\mathrm{TCNQ}^{\bullet-}]}{\mathrm{d}t} = -k_3\,[\mathrm{TCNQ}^0][\mathrm{TCNQ}^{\bullet-}] \tag{5}$$

$$\frac{\mathrm{d}[\mathrm{TCNQ}^0]}{\mathrm{d}t} = +k_3\,[\mathrm{TCNQ}^0][\mathrm{TCNQ}^{\bullet-}] - k_4\,[\mathrm{TCNQ}^0] \tag{6}$$

$$\frac{\mathrm{d}[\mathrm{DCTC}^-]}{\mathrm{d}t} = +k_4\,[\mathrm{TCNQ}^0] \tag{7}$$

where k_3 is a second-order rate constant and k_4 is a pseudo-first-order rate constant describing the oxidation of TCNQ^0. In this scheme, the concentration of the excess nitrite is assumed constant and is taken into the rate constant.

An estimate of k_4 has been obtained from an independent experiment in which TCNQ^0 was used as the starting reactant. Figure 4 shows the first-order plot obtained from the nitrite-induced decomposition of TCNQ^0 from which a value for k_4 of 0.16 min^{-1} is obtained.

The autocatalytic model may be tested by fitting the experimental data (Figure 3). Four solutions of KTCNQ of different initial concentrations (0.1, 0.08, 0.06, and 0.04 mM) were treated with excess aqueous $\mathrm{KNO_2}$ (10 mM). The concentrations of TCNQ^0, $\mathrm{TCNQ}^{\bullet-}$, and DCTC^- were determined, as already described, after 1 min and then at 10-min intervals over a period of 1 h.

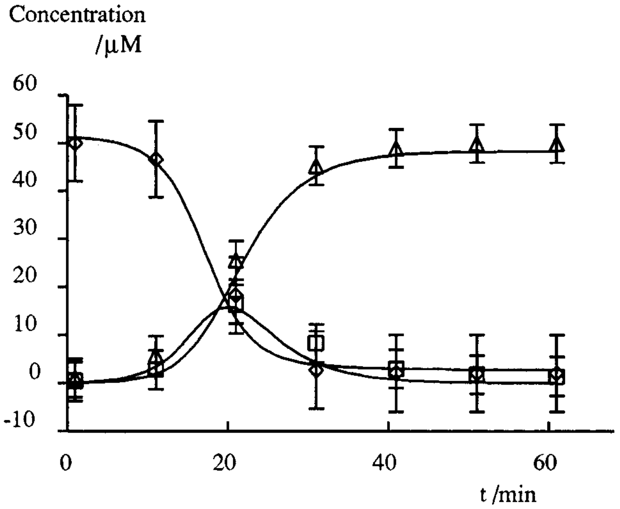

Figure 3. Observed (data points) and calculated (best-fit lines) time-dependence of the concentrations of $\mathrm{TCNQ}^{\bullet-}$ (◇), TCNQ^0 (□), and DCTC^- (△) in the nitrite-induced decomposition of KTCNQ **1**.

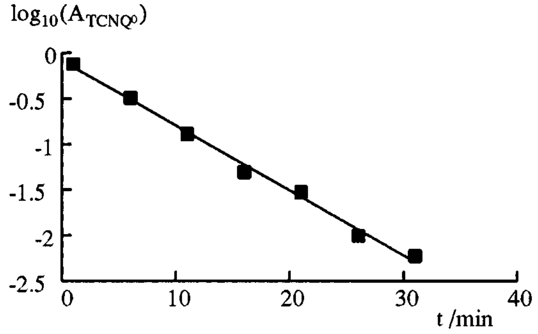

Figure 4. The first-order behavior of the decomposition of TCNQ^0 in the presence of excess nitrite.

Equations 5−7 were integrated numerically by a forward difference method with a time step of 1 min. The initial concentration of $\mathrm{TCNQ}^{\bullet-}$ was known, and the parameters of the model were therefore $[\mathrm{TCNQ}^0]$ at $t = 0$, k_3 and k_4. These values were determined by the "Solver" routine in Microsoft Excel v.5.0, which minimized the following function:

$$F = \sum_{j=1}^{j=3}\sum_{i=1}^{i=7} \frac{([\mathrm{S}_j]_{\mathrm{measured}} - [\mathrm{S}_j]_{\mathrm{calculated}})_i^{\,2}}{u_j^{\,2}} \tag{8}$$

In eq 8, for the i^{th} datum, $[\mathrm{S}j]$ is the concentration of species j and u_j is the standard uncertainty. The weighted function of eq 8 avoids excessive leverage from species for which there is a large uncertainty in the measurement. The error bars in Figure 3 are 95% confidence intervals, with a coverage factor of 2. The solid lines in Figure 3 are the result of a fit to the oxidation of 0.1 mM $\mathrm{TCNQ}^{\bullet-}$.

From the four experiments, we find $k_3 = 1.2 \pm 0.8 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{min}^{-1}$, $k_4 = 0.14 \pm 0.10\ \mathrm{min}^{-1}$, and the equilibrium constant for the initial disproportionation (eq 1) $K_1 = ([\mathrm{TCNQ}^0][\mathrm{TCNQ}^{2-}]/[\mathrm{TCNQ}^{\bullet-}]^2)_{t=0} = 1 \pm 2 \times 10^{-6}$. The interval quoted is the 95% confidence interval. It is seen that the range of values for k_4 encompasses that determined from Figure 4. The value of K is significantly greater than the *approximate* figure of 10^{-9} previously reported.[5] However, the fit is not sensitive to the initial concentration of $TCNQ^0$, and we do not consider this a serious discrepancy.

Conclusions

The relative ease of oxidation of KTCNQ in the presence of [2.2.2]-cryptand contrasts markedly with the behavior of other crown-encapsulated $TCNQ^{\bullet -}$ salts, such as $K^+(15\text{-crown-}5)_2TCNQ^{\bullet -}$, which shows remarkable stability in solution.[21] Interestingly, the latter is most readily prepared by slow crystallization of a 1:1 stoichiometry crown ether:KTCNQ solution, a situation in which the absence of sufficient crown for total ion encapsulation as a $(15\text{-crown-}5)_2K^+$ sandwich means that ion-pair association remains feasible. Cryptate formation precludes such an ion-pair interaction, with a consequent reduction in the stability of $TCNQ^{\bullet -}$ in acetonitrile because the $TCNQ^{\bullet -}$ exists as monomers in this solvent. Further evidence for the effect of ion-pair association on the stability of $TCNQ^{\bullet -}$ salts is currently being sought.

Our kinetic data support an autocatalytic pathway for the nitrite-induced decomposition of $TCNQ^{\bullet -}$ salts in which the presence of $TCNQ^0$ **1** promotes the initial oxidation of $TCNQ^{\bullet -}$ ($\mathbf{1}^{\bullet -}$), a process that is followed by hydrolysis of **1** as outlined in the following equation:

$$\underset{\mathbf{1}}{TCNQ^0} + \underset{\mathbf{1}^{\bullet -}}{TCNQ^{\bullet -}} \xrightarrow[H_2O]{NO_2^-} 2\ \underset{\mathbf{1}}{TCNQ^0} \xrightarrow[H_2O]{NO_2^-} 2\ \underset{\mathbf{2}}{DCTC^-} \qquad (9)$$

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Supporting Information Available: Listings of tables of fractional atomic coordinates, selected interatomic distances, bond and torsion angles, anisotropic temperature factors, and observed and calculated structure factors for **6**, together with additional figures showing crystal packing and the numbering scheme used for the structure solution (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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