from the N+ equation are common and have been attributed to a different mechanism[4] for the addition of water than for the addition of other nucleophiles: general-base catalyzed addition, rather than direct nucleophilic attack (the point for water falls on the Brönsted correlation line based on the other oxyanion catalysts which appear to react via a general-base catalyzed mechanism).

Ritchie reported a slope near 1 when rate constants for the reactions of nucleophiles with 2,4-dinitrochlorobenzene and other 2,4-dinitrohalobenzenes were plotted against the nucleophile's N+ values.[6] We get a slope of 0.95 ± 0.13 (Figure 1), in which data from Ritchie's work[6] and from this study are included in the correlation (rate constants for the reactions promoted by azide ions (in water and methanol) are excluded—see above and ref 6). For the reactions of 2,4-dinitrochlorobenzene, the correlation spans a reactivity range of almost 10^7.

Despite these overall good correlations, there are significant changes in relative nucleophilic reactivities. For example, the piperidine–hydroxide ion rate constant ratio varies from 331 for 2,4-dinitrochlorobenzene to 16 for picryl chloride, and the piperidine–trifluoroethylamine ratio varies from 912 for picryl chloride to 3801 for 2,4-dinitrochlorobenzene. Some of these changes in relative nucleophilic reactivities may be a result of steric effects.[9,10] For example, secondary amines such as piperidine and morpholine are relatively more reactive than less hindered primary amines in reactions with 2,4-dinitrochlorobenzene (e.g., for the reactions of picryl chloride and 2,4-dinitrochlorobenzene the morpholine–semicarbazide and morpholine–methoxylamine ratios are 17 and 363 and 16 and 575, respectively). These effects can not, however, account for the slope of less than one observed for the reactions of picryl chloride, because the slope is not significantly different (0.82 ± 0.11) when the points for the more hindered secondary amines are omitted from the plot.

The slopes less than one observed here for the reactions of picryl chloride (Figure 1) mean that picryl chloride shows a lower selectivity toward nucleophilic attack than does 2,4-dinitrochlorobenzene, in accordance with the reactivity–selectivity principle and with relative nucleophilic reactivities that are substrate dependent.

Cyclodextrin Complexation of the Tetracyanoquinodimethane Anion Radical: The Chemical Consequences of Cavity Size and Alkyl Derivatization

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Optical spectroscopy shows that in aqueous solution the tetracyanoquinodimethane anion radical ($TCNQ^-$) exists in equilibrium with its π–π dimer (Boyd and Phillips). A study of the effect of various cyclodextrins on this equilibrium shows strikingly different results depending on cavity size and on alkyl derivatization. The equilibrium is unaffected by the presence of α-cyclodextrin. In contrast, γ-cyclodextrin complexes and stabilizes the π–π dimer. EPR and optical spectroscopy show that the anion radical is included and stabilized by heptakis(2,6-di-*o*-methyl)-β-cyclodextrin and a 2-hydroxypropyl derivative of β-cyclodextrin. Of great interest is the observation that the complex formed by $TCNQ^-$ and β-cyclodextrin rapidly reacts to form a diamagnetic product. Aqueous solutions of this diamagnetic product give evidence of appreciable concentrations of $TCNQ^-$ when heated or when low dielectric solvents like methanol are added. NMR indicates that the diamagnetic product is a dianion formed by the σ bonding of two β-cyclodextrin complexed anion radicals. σ-Bonded dimers of $TCNQ^-$ have been previously observed only in the solid phase (Vu Dong et al., Harms et al.). The tetrafluorotetracyanoquinodimethane anion radical exhibits the same general cyclodextrin chemistry as $TCNQ^-$.

Introduction

Here we describe the interesting aqueous chemistry of the tetracyanoquinodimethane anion radical ($TCNQ^-$) in the presence of cyclodextrins, in particular the formation of a dimer upon inclusion in β-cyclodextrin. Cyclodextrins (CDs) are α-1,4-linked cyclic oligomers of D-glucopyranose that form inclusion complexes with a variety of small molecules. The ability of the cyclodextrins to form complexes with nitroxide radicals in aqueous solution is well-known and has been investigated by EPR, NMR, and electrochemistry.[1-5] Other free radicals, such as the radical intermediate of the nitrophenolate anion and the benzosemiquinone radical anion, which are stable in aqueous solution, also form cyclodextrin complexes.[6,7] The aqueous chemistry of $TCNQ^-$ alone was studied by Boyd and Phillips who reported the reversible dimerization of $TCNQ^-$ in water and used optical spectroscopy to determine the equilibrium constant (2.5×10^3 at 298 K) and the enthalpy of dimerization (−10.4 kcal/mol) associated with the reaction[8]

$$2TCNQ^- \rightleftharpoons (TCNQ)_2^{2-} \quad (1)$$

† American Chemical Society—Petroleum Research Fund Scholar.

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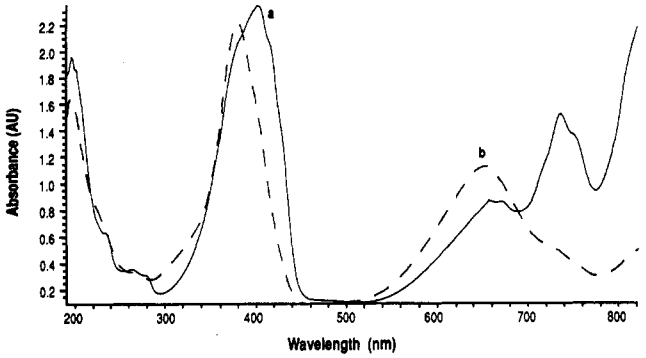

Figure 1. Optical spectra, aqueous solutions at 298 K: (a) 10^{-4} M LiTCNQ; (b) 5.0×10^{-5} M γ-CD/10^{-4} M LiTCNQ.

Their experiments near room temperature were made relatively easy by the stability of $TCNQ^-$ at pH 7 in an oxygen-free solution; experiments in other solvents such as methanol and *N,N*-dimethylformamide showed no evidence of dimerization. These observations indicate that specific solvation effects are important in stabilizing the dimer. Other studies of the effect of solvent on (1) confirmed the results of Boyd and Phillips and showed that in pure water the identity of the alkali metal cation had no effect on the dimerization. In solutions containing more than 50% ethanol, dimerization can no longer be observed.[9]

Experimental Section

The α-, β-, and γ-CDs (Advanced Separation Technologies Inc., Whippany, NJ) and heptakis(2,6-di-*o*-methyl)-β-cyclodextrin (Aldrich Chemical Co., Milwaukee, WI) were used as received. "Molecusol", a 2-hydroxypropyl derivative of β-cyclodextrin, was obtained from the manufacturer, Pharmatec Inc., Alachua, FL. Tetrafluorotetracyanoquinodimethane (FTCNQ) (TCI American, Portland, OR) and TCNQ (Aldrich Chemical Co., Milwaukee, WI) served as the starting materials for the synthesis of the alkali metal salts of $FTCNQ^-$ and $TCNQ^-$.[10] The synthesis of *p*-phenylenedimalonitrile was carried out using the approach of Acker and Hertler.[11]

A Hewlett-Packard Model 8452 diode array spectrometer was used for measuring optical spectra; optical cells with pathlengths of 0.1–1.0 cm were used for determining optical spectra. In preparing samples, all solvents were degassed (by vacuum techniques) or deoxygenated (by bubbling N_2) before the alkali metal salts were added.

EPR experiments were carried out on a Varian EM500. This instrument was designed for instructional purposes and lacks many of the field and microwave calibration capabilities of a research-grade instrument. Oxygen was removed from the EPR samples by the same techniques used for the samples studied optically.

NMR spectra were obtained on a Varian GEMINI-200 spectrometer at frequencies of 200.0 MHz for ^1H and 50.3 MHz for ^{13}C. The 90° pulses are 22.5 μs for ^1H and 21 μs for ^{13}C. Relaxation delays of 1 s were used. Proton and carbon assignments were obtained from 2-D heteronuclear correlation spectra, HETCOR, and homonuclear *J*-resolved 2-D spectra, HOM2DJ,[12-16] acquired at 25 °C. The GEMINI is equipped with a variable-temperature controller and probe.

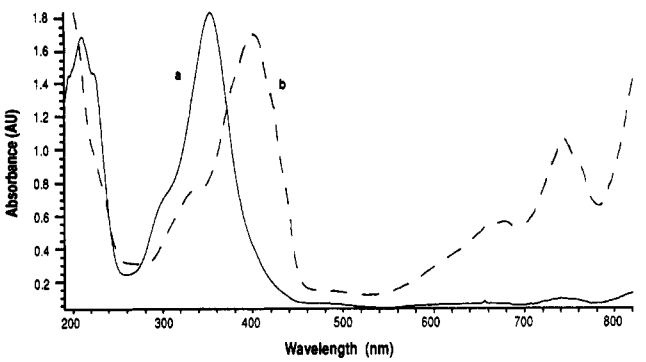

Figure 2. Optical spectra, aqueous solutions at 298 K: (a) 10^{-4} M β-CD/10^{-4} M LiTCNQ; (b) 10^{-4} M Molecusol/10^{-4} M LiTCNQ.

In the course of the NMR studies a dilution experiment was carried out in which $TCNQ^-$ was added (as LiTCNQ) to a 2.5×10^{-2} M β-cyclodextrin solution in D_2O to yield $TCNQ^-$ concentrations of 0.5×10^{-2}, 1.0×10^{-2}, 1.5×10^{-2}, 2.0×10^{-2}, and 2.5×10^{-2} M. Spectra were obtained in 2610 scans for ^{13}C and 300 scans for ^1H. The 2-D studies were carried out on solutions that were 2.5×10^{-2} M $TCNQ^-$/2.5×10^{-2} M β-cyclodextrin.

Results

Figure 1 shows the optical spectrum of a 10^{-4} M blue-green aqueous solution of LiTCNQ. Following Boyd and Phillips the anion radical is assigned an absorption maximum at 737 nm and the dimer at 643 nm. Variable-temperature optical experiments yield $K = 2.7 \times 10^3$ at 298 K and $\Delta H_{dimerizn} = -10.3 \pm 0.3$ kcal for (1); these are in excellent agreement with the literature.

The addition of 5-fold excess of α-CD to a 10^{-4} M solution of $TCNQ^-$ produces no change in the optical spectrum. The addition of γ-CD to a solution of $TCNQ^-$ leads to a decrease in the intensity of the monomer peak and an increase in the intensity of the dimer peak. Figure 1 shows the spectrum of a dark blue solution of 5×10^{-5} M γ-CD and 10^{-4} M $TCNQ^-$; the peak due to the dimer dominates. An accurate determination of the formation constant for the γ-CD-dimer complex has proven difficult; however, our optical experiments do clearly indicate a value >1000. Clarke et al. reported on the Roccellin monomer–dimer equilibrium and on complexation of the dimer by γ-CD and the monomer by β-CD. They also discussed the problems associated with the determination of accurate formation constants for such complexes.[17]

The addition of Molecusol to a solution of $TCNQ^-$ leads to a decrease in the intensity of the dimer peak relative to the monomer peak. Figure 2 shows the spectrum from a solution of 10^{-4} M Molecusol and 10^{-4} M $TCNQ^-$. Further increasing the Molecusol concentration leads to the complete disappearance of the dimer peak. An essentially identical result is obtained when heptakis(2,6-di-*o*-methyl)-β-CD is used instead of Molecusol as the complexing agent. Surprisingly, β-CD produces very different changes in the optical spectrum of $TCNQ^-$ from those discussed above. Figure 2 shows the spectrum from a solution containing 10^{-4} M β-CD and 10^{-4} M $TCNQ^-$; here, a band centered at 355 nm dominates the spectrum with a band at about 740 nm having an intensity slightly above background. The results of the above optical experiments suggest that, while β-CD may form a complex with $TCNQ^-$, that complex is unstable relative to an aromatic product differing substantially in molecular structure from $TCNQ^-$.

Further insight may be gained from EPR. Figure 3 shows the EPR spectrum from a 7.0×10^{-3} M solution of

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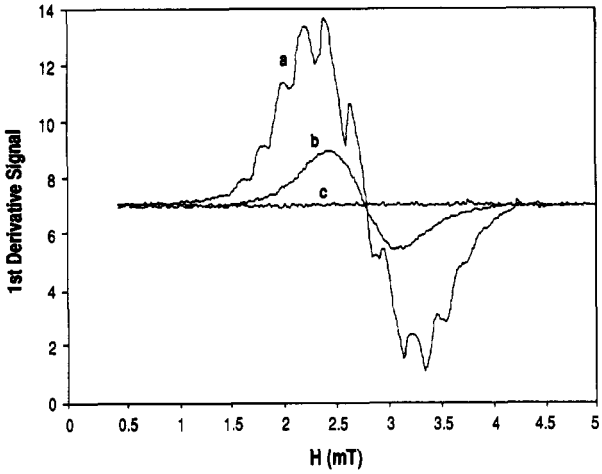

Figure 3. EPR spectra, aqueous solutions at 298 K: (a) 7.0×10^{-3} M LiTCNQ/1.4×10^{-3} M Molecusol; (b) 7.0×10^{-3} M LiTCNQ; (c) 7.0×10^{-3} M LiTCNQ/7.0×10^{-3} M β-CD.

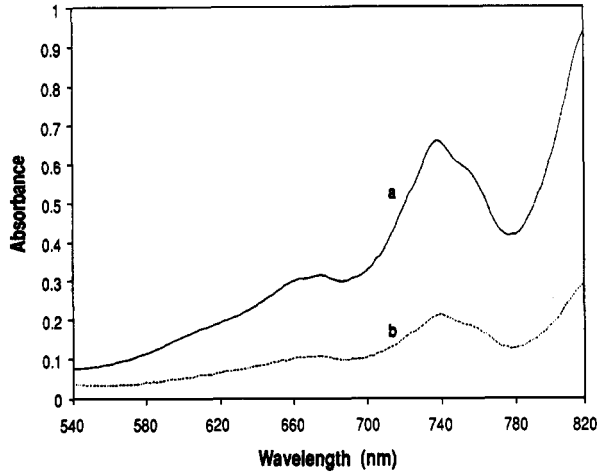

Figure 4. Optical spectra, aqueous solutions of 10^{-3} M LiTCNQ/10^{-3} M β-CD: (a) 40 °C; (b) 25 °C.

TCNQ⁻ before and after the addition of 1.4×10^{-2} M Molecusol. In the absence of the cyclodextrin, Heisenberg exchange (arising from TCNQ⁻ collisions) and chemical exchange (arising from (1)) lead to a single exchange narrowed peak for the TCNQ⁻ radical. As suggested by the optical experiments, Molecusol complexes the radical and shifts (1) to produce a more intense EPR signal; in addition, reduced exchange effects lead to resolved hyperfine splittings. The reduction of Heisenberg spin exchange rates due to cyclodextrin complexation has been previously investigated for the nitroxides.[18] The integrated intensity of the Molecusol-complexed TCNQ⁻ spectrum in Figure 3 is about a factor of 5 more intense than that of the radical in the absence of cyclodextrin. The ratio of integrated intensities expected on the basis of the equilibrium constant for (1) and complete complexation by Molecusol is 6.4. The difference between theory and experiment may arise from reaction of a portion of the radicals with minor impurities in the Molecusol or perhaps the precipitation of a small amount of complex (see below). The EPR results obtained using (2,6-di-*o*-methyl)-β-CD are qualitatively similar to those for the Molecusol except the signal from the CD-complexed TCNQ⁻ is only 2–3 times that for the radical alone. Here, addition of CD to the TCNQ⁻ sample was accompanied by the formation of a green precipitate which could be observed visually. The cyclodextrin in this precipitate might be either the (2,6-di-*o*-methyl)-β-CD or perhaps a CD with a higher degree of methyl group substitution. Such highly substituted analogs are probable impurities in commercial samples of (2,6-di-*o*-methyl)-β-CD. No EPR spectrum could be observed from solutions containing 7.0×10^{-3} M TCNQ⁻ and 1.4×10^{-2} M β-CD. However, in extremely concentrated solutions containing 2.0×10^{-2} M β-CD and 1.8×10^{-2} M TCNQ⁻ a weak single-line spectrum could be observed, indicating that the formation of diamagnetic product is a reversible process. Furthermore, at 40 °C a 10^{-3} M solution of TCNQ⁻ and 10^{-3} M β-CD produced an optical spectrum (Figure 4) which showed clearly the presence of TCNQ⁻, where at 20 °C there is only a trace of a monomer absorbance band. The shape of the absorbance peak at 740 nm is identical to that of the complexed TCNQ⁻.

For FTCNQ⁻, experiments similar to those of Boyd and Phillips showed the existence of a monomer, π–π dimer equilibrium, and gave $K = 1.1 \times 10^3$ at 298 K with $\Delta H_{\text{dimerizn}} = -14.3 \pm 0.5$ kcal. Optical and EPR experiments like those described above showed that the cyclodextrin chemistry of FTCNQ⁻ is qualitatively similar to that of TCNQ⁻. Addition of methanol or other low dielectric constant solvents to aqueous solutions of β-CD and TCNQ⁻ or FTCNQ⁻ produced rapid and essentially complete conversion of the diamagnetic product to free radical.

Table I. ^{1}H and ^{13}C NMR Chemical Shift Values for β-Cyclodextrin and [TCNQ⁻/β-Cyclodextrin] in D_2O. Values Are Relative to TMS

position	sample	^{13}C	^{1}H	J_{HH}
1	CD	104.81	5.11	$J_{1,2} = 3.8$
	T/CD	105.97	4.97	$J_{1,2} = 4.0$
2	CD	75.04	3.70	$J_{1,2} = 3.8$, $J_{2,3} = 10.1$
	T/CD	75.37	3.43	$J_{1,2} = 4.0$, $J_{2,3} = 10.0$
3	CD	76.04	4.00	$J_{2,3} = 10.5$, $J_{3,4} = 8.7$
	T/CD	75.94	3.88	$J_{2,3} = 10$, $J_{3,4} = 10$
4	CD	84.11	ND	
	T/CD	83.96	3.54	
5	CD	74.81	3.90	
	T/CD	74.83	3.54	
6	CD	63.28	3.92	
	T/CD	62.67	3.87	
p	T/CD	129.5		
	T/CD	147.7		
o or *m*	T/CD		6.95	$J_{o,m} = 10.0$
	T/CD		7.65	$J_{o,m} = 8.0$
o or *m*	T/CD	130.6		$J_{CH} = 158.5$
	T/CD	121.5		$J_{CH} = 158.9$
CN	T/CD	113.8		
CN	T/CD	117.5		

The results of the NMR experiments to determine the nature of the product formed when TCNQ⁻ is added to β-cyclodextrin show the appearance of an A_2X_2 spin system in the downfield region of the ^{1}H spectrum. This indicates the presence of an aromatic species with nonequivalent para substituents. A ^{13}C NMR study in which increasing amounts of TCNQ⁻ are added to a D_2O solution of β-cyclodextrin shows the appearance of new peaks which increase in intensity in direct proportion to the amount of added TCNQ⁻. These new peaks are attributed to the [TCNQ⁻/β-cyclodextrin] diamagnetic product. As the new peaks increase in size the corresponding peaks of β-cyclodextrin decrease in intensity. The frequencies of the new peaks do not change as the ratio of TCNQ⁻/β-cyclodextrin is increased. The series of ^{13}C spectra from this study are shown in Figure 5. The new peaks represent frequency changes greater than +0.3 ppm for C1 and C2 of β-cyclodextrin and a shift of −0.6 ppm for C6. The ^{13}C chemical shift values for β-cyclodextrin and the

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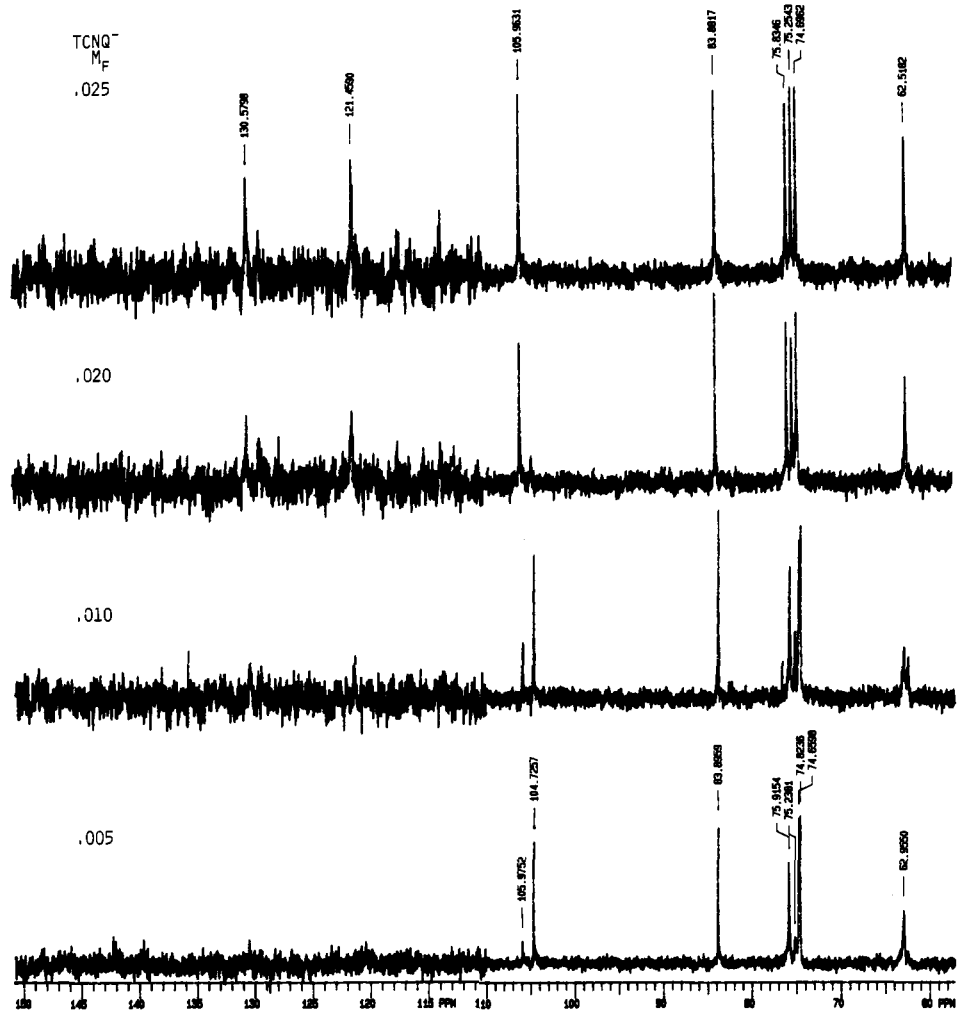

Figure 5. ^{13}C NMR spectra, aqueous solutions, 298 K, dilution study of 2.5×10^{-2} M β-CD with 0.5×10^{-2}, 1.0×10^{-2}, 1.5×10^{-2}, 2.0×10^{-2}, and 2.5×10^{-2} M LiTCNQ. (Downfield region is plotted with an enhanced amplitude.)

[$TCNQ^-$/β-cyclodextrin] product are given in Table I.

Peaks attributed to a diamagnetic species of TCNQ appear in the aromatic region of the ^{13}C spectra of [$TCNQ^-$/β-cyclodextrin]. These peak frequencies are given in Table I. Comparison of ^1H-decoupled and ^1H-coupled ^{13}C-spectra of [$TCNQ^-$/β-cyclodextrin] show that peaks at 130.60 and 121.5 ppm are due to carbons with attached protons while those at 147.7, 129.5, 117.5, and 113.8 ppm show no H-splitting, indicating the absence of an attached H. The H-attached carbons are attributed to the ortho and meta positions of an aromatic ring and the non-H substituted carbons are the para and CN carbons.

The ^{13}C-chemical shifts of synthesized *p*-phenylenedimalonitrile show similarities with the values observed for complexed $TCNQ^-$. The aromatic peaks of *p*-phenylenedimalonitrile fall at 133.8 ppm for the ortho and meta positions and 133.0 ppm for substituted para positions. In comparison the values for the ortho and meta positions of complexed TCNQ are 121.5 and 130.6 ppm and for the substituted carbons are 147.7 and 129.5 ppm. These results support the conclusion that the two ends of the complexed $TCNQ^-$ are not equivalent. The cyano carbons fall at 119.7 ppm for *p*-phenylenedimalononitrile and 117.5 and 113.8 ppm for complexed $TCNQ^-$. This indicates two environments for the four CN's of complexed TCNQ. The 117.5 ppm peak is broadened relative to the 113.8 ppm peak indicating slightly differing chemical shifts for the CN's contributing to the 117.5 ppm peak.

The proton spectra confirm the results presented above. Figure 6 displays the proton spectra obtained from the sequential dilution study described for Figure 5. The obvious changes are the disappearance of the H1 peak at 5.02 ppm and the appearance of the peak at 4.96 ppm. In the aromatic region, doublets at 7.63 and 6.96 ppm appear. These are attributed to the diamagnetic TCNQ species. Changes in the upfield region have been elucidated using 2-D NMR techniques. Results from HETCOR and HOMO2DJ experiments have yielded the assignments of the proton peaks. Figures 7 and 8 show the HETCOR results of β-cyclodextrin and [$TCNQ^-$/β-cyclodextrin], respectively. The HOMO2DJ results are shown in Figure 9. The ^1H chemical shift values for β-cyclodextrin and [$TCNQ^-$/β-cyclodextrin] are given in Table I.

Discussion

Optical spectroscopy shows that under the conditions of our experiments neither α-CD for γ-CD forms an inclusion complex with $TCNQ^-$. However, γ-CD, unlike α-CD, does form a complex with the π–π dimer. EPR and optical experiments, in which Molecusol or heptakis(2,6-di-*o*-methyl)-β-CD are added to aqueous solutions of $TCNQ^-$, show that derivatized β-CDs can readily complex the $TCNQ^-$ anion radical and that the resulting complex is stable. However, optical, NMR, and EPR results indicate that the product of the reaction which occurs when β-CD is added to an aqueous solution of $TCNQ^-$ is not a free radical. Optical spectra at several temperatures and EPR results at high concentrations of β-CD and $TCNQ^-$ suggest that the β-CD-complexed $TCNQ^-$ radial can exist in equilibrium with the diamagnetic product. The NMR

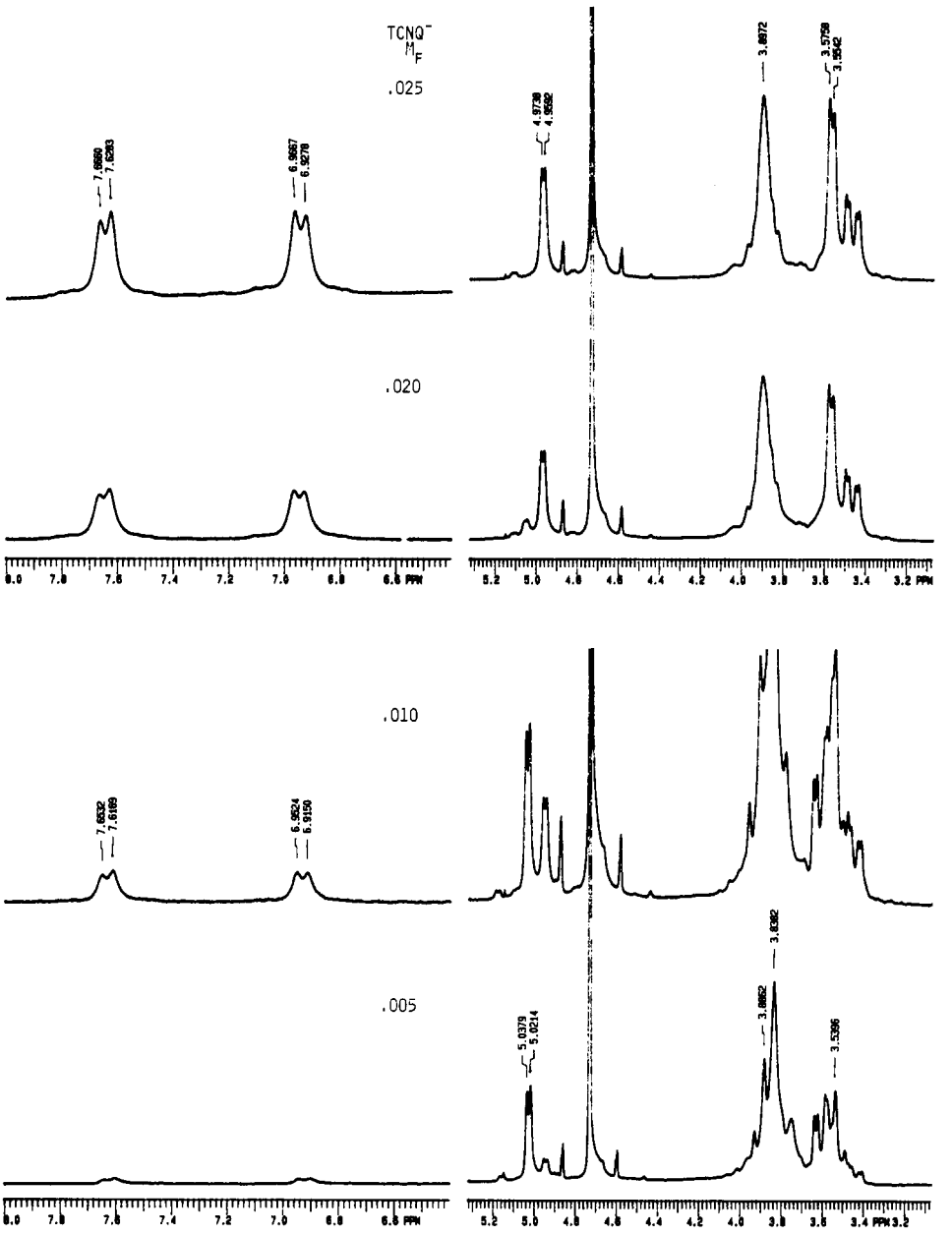

Figure 6. Proton NMR spectra, aqueous solutions, 298 K, dilution study of 2.5×10^{-2} M β-CD with 0.5×10^{-2}, 1.0×10^{-2}, 1.5×10^{-2}, 2.0×10^{-2}, and 2.5×10^{-2} M LiTCNQ.

experiments provide insight into the structure of the product.

There are similarities between the NMR results due to complexation of $TCNQ^-$ with β-cyclodextrin and those reported for other inclusion complexes with cyclodextrins. In this study, the observed complexation-induced shifts of β-cyclodextrin protons H1, H3, and H5 were −0.14, 0.12 and −0.36 ppm, respectively, where negative indicates upfield. In comparison, published studies of naphthalenes complexed with β-cyclodextrin yield upper limits on observed complexation-induced shifts for H3 and H5 of 0.12 and 0.25 ppm, respectively.[19] Complexation of para-substituted phenols with β-cyclodextrin has been shown[20] to induce shifts of −0.07 to −0.16 ppm for H3 and −0.19 to −0.23 ppm for H5. The induced shifts that are observed for [$TCNQ^-$/β-cyclodextrin] are similar to those observed for para-substituted phenols while the changes in H-3 and H-5 differ dramatically from the values observed upon complexation of naphthalene.

Shifts of the guest ^1H and ^{13}C also occur upon complexation. The reported[19] complexation-induced ^1H shifts of the guest molecules 2-toluidino-6-naphthalenesulfonae (TNS) and 1-anilino-8-naphthalenesulfonate (ANS) in β-cyclodextrin are −0.04 to −0.48 ppm and −0.04 to −0.11 ppm, respectively. The proton spectrum of free $TCNQ^-$ is not interpretable. However, the shift difference between the aromatic protons of the complexed $TCNQ^-$ is 0.7 ppm. The size of this shift is too large to attribute to inclusion alone and indicates that the two positions are chemically different.

Inoue et al. reported the complexation-induced ^{13}C shifts for the guests phenylalanine[21] and *p*-nitrophenol[22] in β-cyclodextrin. These studies are not ideal comparisons since the former complex was prepared in 1 M NaOH and the

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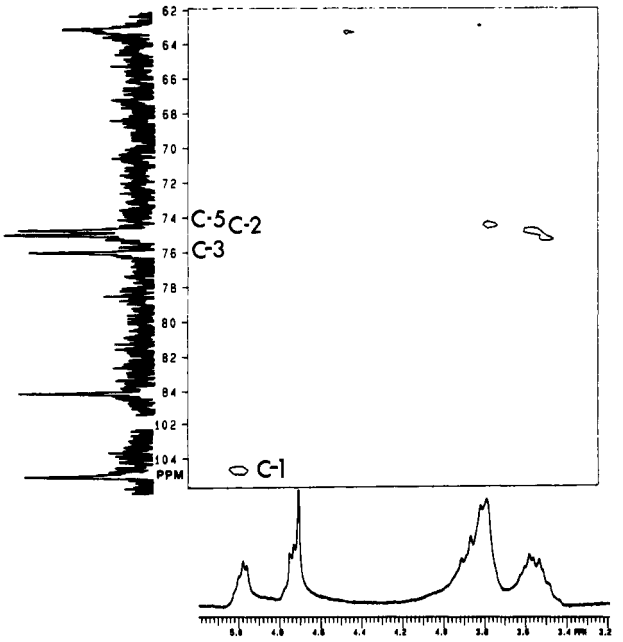


Figure 7. HETCOR spectrum, 298 K, aqueous solution of 2.5 × 10^{-2} M β-CD.

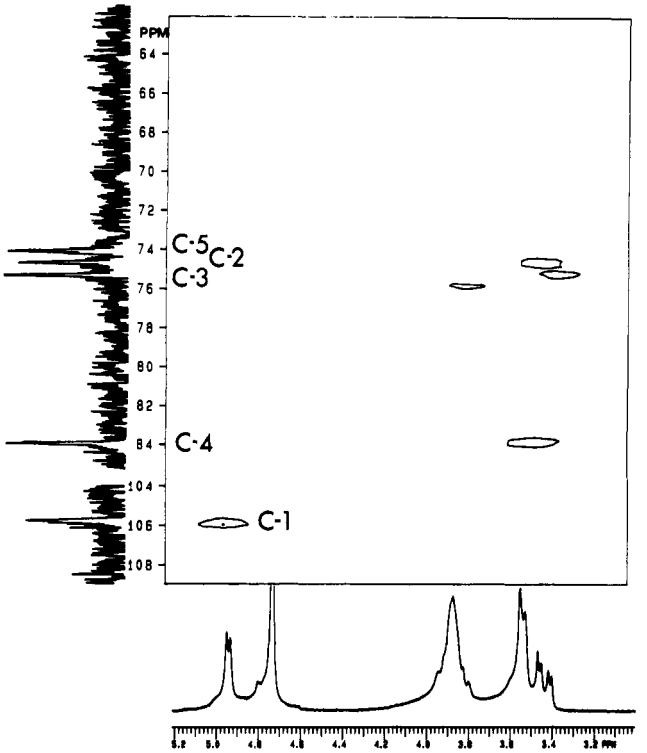


Figure 8. HETCOR spectrum, 298 K, aqueous solution of 2.5 × 10^{-2} M LiTCNQ/2.5 × 10^{-2} M β-CD.

latter was solid. The shifts induced in ring carbons C2 and C4 of phenylalanine were −0.36 and 0.36 ppm, respectively. The induced shifts in *p*-nitrophenol positions C1, C2, C3 and C4 were −1.4, −1.6, −1.7, and 0.6 ppm, respectively. Since it was not possible to observe ^{13}C spectra of free $TCNQ^-$, we are unable to determine induced shifts in the ^{13}C values of the product. What we are able to say is that the carbon shifts of the ortho and meta positions in the included $TCNQ^-$ differ by 9.1 ppm. Before complexation of $TCNQ^-$, these two positions are expected to be equivalent. Thus, product formation has induced a maximum possible change of 9.1 ppm. This is larger by a factor of 3 than any ^{13}C shift reported for inclusion complexes. The substituted carbons differ by 18.2 ppm. Such a large

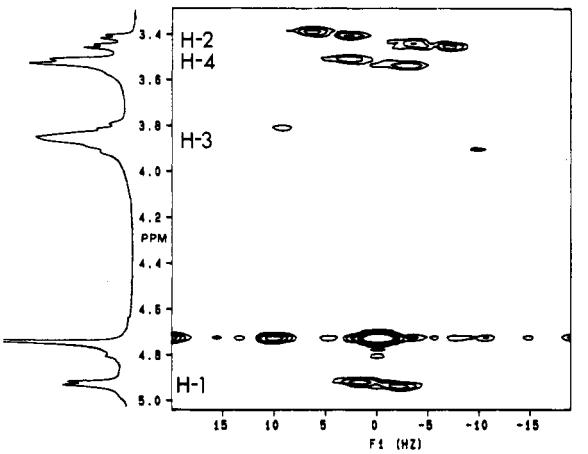
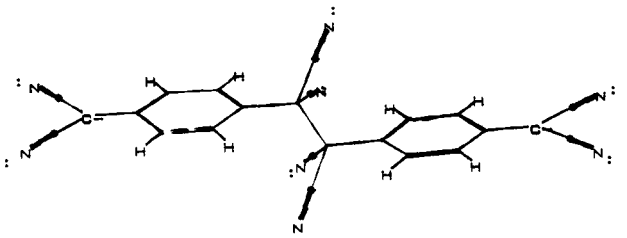


Figure 9. HOMO2DJ spectrum, 298 K, aqueous solution of 2.5 × 10^{-2} M β-CD and 2.5 × 10^{-2} M LiTCNQ.

change can only by attributed to chemically distinct carbons.

There is a striking contrast between the results of [$TCNQ^-$/β-cyclodextrin] NMR studies and previously referenced studies of inclusion complexes. In the latter studies, the original NMR lines due to β-cyclodextrin shift continuously as the concentration of included organic is increased. This is consistent with fast exchange of β-cyclodextrin on and off the included molecule. In contrast, as $TCNQ^-$ is added to a solution of β-cyclodextrin, new [$TCNQ^-$/β-cyclodextrin] complex peaks appear in the presence of the original β-cyclodextrin peaks. This behavior is consistent with a very slow exchange of β-cyclodextrin between the complexed and free state. Elementary exchange theory[23] places this exchange below 30 s^{-1} for a peak separation of 15 Hz. This process will be discussed in detail in a future publication.[24]

The NMR thus indicates that the product formed when β-CD is added to an aqueous solution of $TCNQ^-$ is a cyclodextrin-complexed σ-bonded dimer with the molecular structure



A similar σ-bonded structure was reported for $TCNQ^-$ in the solid phase.[25-27] There are three possible isomers for the cyclodextrin-complexed dimer; NMR spectra indicate the presence of only one. The most likely structure for this isomer is one where the secondary glucopyranose hydroxyls on the two cyclodextrins face each other.

On the basis of the observation that derivatized β-CDs form stable complexes with $TCNQ^-$ and that β-CD-complexed $TCNQ^-$ can be observed in equilibrium with the σ-bonded dimer, the following mechanism is suggested:

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$$\beta CD + TCNQ^- \rightleftharpoons (\beta CD\text{–}TCNQ^-) \quad (2)$$

$$2(\beta CD\text{–}TCNQ^-) = (\beta CD\text{–}TCNQ)_2^{2-} \quad (3)$$

Derivatization of β-CD blocks the formation of σ-bonded dimer; presumably this occurs because two derivatized β-CDs with $TCNQ^-$ included cannot approach each other closely enough for a σ-bond to form. By use of the Van't Hoff equation and the data from Figure 4, an approximate value for the ΔH of reaction (3) was determined to be −100 kJ.

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Photo-CIDNP and Nanosecond Laser Flash Photolysis Studies on the Photodecomposition of Triarylsulfonium Salts

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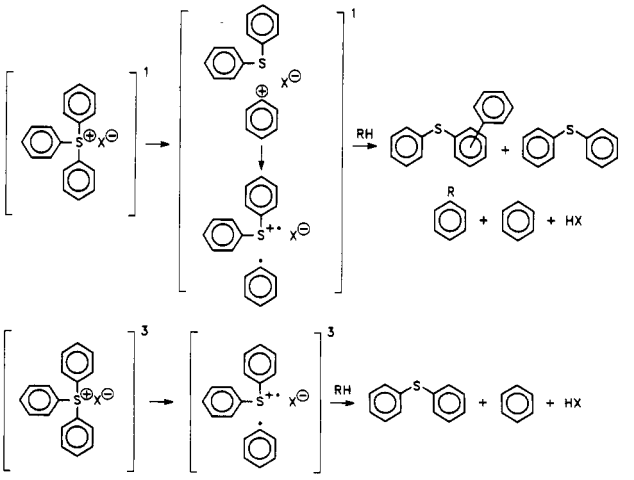
The direct and sensitized photodecomposition of triarylsulfonium salts have been investigated by nanosecond laser flash photolysis and steady-state photo-CIDNP. The direct photoreaction of triphenylsulfonium salts was shown to proceed via a singlet diphenylsulfinyl radical cation–phenyl radical pair which is produced by internal electron transfer from the initially formed phenyl cation–diphenyl sulfide pair. Recombination of both sets of intermediates gives protonated (phenylthio)biphenyls, identified as a broad transient absorption centered at 465 nm, which lose H^+ to give 2-, 3-, and 4-(phenylthio)biphenyl. The acetone-sensitized photoreaction gave a triplet excited state of the salt, which then dissociated to give the triplet diphenylsulfinyl radical cation (λ_{max} 750, 340 nm)–phenyl radical pair and subsequently underwent escape reactions with the solvent. Anthracene-, 9,10-diphenylanthracene-, naphthalene-, and perylene-sensitized photoreactions of triphenylsulfonium salts proceeded by electron transfer from the singlet excited state of the aromatic hydrocarbon to give the singlet aromatic hydrocarbon radical cation–triphenylsulfur radical pair, which dissociates to the in-cage triad of diphenyl sulfide, phenyl radical, and the aromatic hydrocarbon radical cation. In the solvent cage naphthalene radical cation can oxidize diphenyl sulfide to diphenylsulfinyl radical cation, identified by transient absorptions at 750 and 340 nm, whereas the other hydrocarbon radical cations cannot. In contrast to the triphenylsulfonium salts, the [(phenylthio)phenyl]diphenylsulfonium salt decomposed via the triplet excited state upon both direct and triplet-sensitized photolysis. Photo-CIDNP gave a strong enhanced absorption which was quenched upon the addition of oxygen and also gave transients, identified as diphenylsulfinyl radical cation (λ_{max} 750, 340 nm), upon both direct and triplet-sensitized photolysis.

Introduction

In recent years the onium salts of sulfur and iodine have found extensive application as photochemical polymerization initiators.[2] These onium salts have proven to be especially useful as photochemical sources of protic acid, which can then induce polymerization of a wide variety of monomers or defunctionalize acid-sensitive groups attached to polymers. Because of their great importance, a number of studies dealing with the photodecomposition of onium salts have appeared in the literature.[2-9] The photochemistry of these salts is quite complex due to the fact that both in-cage and cage-escape reaction products

Scheme I. Photodecomposition Pathways for Triphenylsulfonium Salts from the Singlet and Triplet Excited States



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