

Charge-Transfer Interaction between Tetracyanoethylene and Pyridines¹H. J. SHINE AND R. D. GOODIN²*Department of Chemistry, Texas Technological College, Lubbock, Texas 79409**Received August 14, 1969*

The absorption peak at 400 nm sometimes attributed to charge-transfer complexes between tetracyanoethylene (TCNE) and pyridines is in fact caused by the pentacyanopropenide ion. Broad bands which are formed in the region of 340–350 nm when TCNE reacts with pyridine, 4-picoline, 3,4-lutidine, and 3,5-lutidine are now attributed to charge transfer. The bands become distorted and overshadowed in time by absorption owing to formation of the pentacyanopropenide ion and also of the TCNE anion radical. Charge transfer between TCNE and 2-picoline and TCNE and 2,6-lutidine could not be detected. The indications are that charge transfer is of the $n-\pi$ type.

Tetracyanoethylene (TCNE) forms charge-transfer complexes with aromatic π donors, and this type of interaction has been extensively studied.^{3–5} Comparatively little work, however, has been reported on TCNE complexes with n -electron donors. In many of the systems using n -electron donors that have been studied, the presence of the TCNE anion radical has been detected by electron spin resonance and optical spectroscopy. In most of these instances, radical formation was attributed to dissociation of the charge-transfer complex with complete one-electron transfer.^{6,7} Very few workers, however, have shown conclusive evidence for the presence of the corresponding cation radical, necessarily formed by this dissociation. In studies of complexes between TCNE and heteroatomic donors by spectrophotometric methods, most workers report reactions which make complex detection difficult.

Pyridine, which may conceivably act either as an n - or π -electron donor, was first treated with TCNE by Merrifield and Phillips⁸ in 1958. The optical spectrum obtained by these workers showed a doublet at 400 and 421.5 nm which was attributed to the formation of a complex. A Benesi-Hildebrand-type plot of absorbance data for these maxima gave an equilibrium constant of 12.0 for the complex.

Also in 1958, Middleton and coworkers⁹ published their results on the reaction of TCNE with aqueous pyridine. They observed the formation of pyridinium 1,1,2,3,3-pentacyanopropenide in 81% yield. The reaction was not unique to pyridine, and basic hydrolysis of TCNE produced similar salts with several bases studied. Hydrolysis in neutral or acidic solution, however, produced only tricyanoethanol, which was isolated as the tetramethylammonium salt.

The optical spectrum of the pentacyanopropenide ion in water showed a doublet at 393 and 412 nm.⁹

The tricyanoethenolate ion exhibited a single band at 297 nm.¹⁰

Nepras and Zahradnik¹¹ studied the reaction of TCNE with pyridine and a series of nitrogen heteroaromatic donors. These authors stated that the TCNE-pyridine systems yielded a yellow color, erroneously attributed by Merrifield and Phillips to the charge-transfer complex, but Nepras and Zahradnik did not identify the species responsible for the color. The reaction with pyridine was so rapid that no complex could be detected.

In an esr investigation, Pen'kovskii¹² detected the presence of the TCNE anion radical when TCNE was dissolved in pyridine. Pen'kovskii attributed this radical-anion formation to one-electron transfer from pyridine to TCNE.

Farcasiu and Nicolau¹³ have carried out a spectrophotometric study of the molecular complexes formed from TCNE and substituted pyridines in chloroform. Their donor series included pyridine, 2-picoline, 3-picoline, 4-picoline, 2,6-lutidine, and 2,4,6-collidine. The λ_{\max} for each complex was chosen as the 400-nm peak of a doublet, and equilibrium constants were calculated from absorbances at this wavelength.

Middleton observed that the pentacyanopropenide ion is formed in the reaction of TCNE with aqueous pyridine, and that this ion absorbs at 393 and 412 nm.⁹ Therefore, it is probable that the reported complexes of TCNE with pyridine and its derivatives^{8,13} were only observations of the formation of the pentacyanopropenide ion.

The present paper describes what we consider to be charge-transfer bands between TCNE and pyridine and TCNE and some methylpyridines.

In an attempt to determine the source of the TCNE anion radical which is present in these systems, the reduction of TCNE was also investigated.

Water reacts with the TCNE anion radical to form the tricyanoethenolate ion¹⁴ and with TCNE, in the presence of a base, to form the pentacyanopropenide ion.⁹ The TCNE anion radical also reacts with oxygen to produce both pentacyanopropenide and tricyanoethenolate ions.¹⁴ To minimize the interference of these reaction products with complex formation, the

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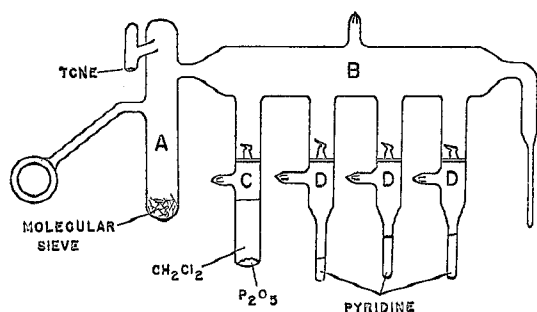


Figure 1.—Apparatus for the detection of charge transfer between TCNE and pyridine donors.

reactions were carried out in a sealed vacuum system under anhydrous conditions.

Experimental Section

Materials.—TCNE (Aldrich Chemical Co.) was crystallized from 1,2-dichloroethane¹⁵ and sublimed under vacuum at 90°. The product was stable for months in a stoppered vial. Pyridine (Matheson, analyzed reagent grade) and the methylpyridines (Aldrich) were refluxed over calcium hydride for several hours, fractionally distilled from the hydride, and stored over fresh calcium hydride until used. Methylene chloride was refluxed over phosphorus pentoxide, distilled from the pentoxide, and stored in a septum-capped flask, from which it was withdrawn by syringe as needed.

Pyridinium 1,1,2,3,3-pentacyanopropenide and tetramethylammonium tricyanoethenolate were prepared by Middleton's procedures.⁹ These salts were used for characterizing the anions spectroscopically.

Potassium Tetracyanoethylenide.¹⁰—Potassium cyanide was crystallized from water-ethanol to remove carbonate and dried in a pistol at 95° for 2 hr before use. Acetonitrile was Distillation Products anhydrous, septum-capped grade. A vacuum-line apparatus was constructed consisting of three chambers, one of which was separated from the other two by a sintered-glass disk. Potassium cyanide (2.65 g), some Linde 3A Molecular Sieve, and 50 ml of acetonitrile were placed in the first chamber. TCNE (5.1 g) was placed in the second chamber. The apparatus was connected to the high vacuum line and the acetonitrile was degassed by freeze-thaw cycles. The apparatus was sealed under vacuum with a torch. The suspension of potassium cyanide in acetonitrile was cooled to -5° and poured onto the TCNE. The solution bubbled violently and became very dark. After it had been stirred magnetically for 2 hr the solution was filtered through the sinter into the third chamber. A bronze solid precipitated overnight. The covering liquid was poured back through the sinter into the second chamber. The solid in the third chamber was washed several times by distilling fresh solvent from, and pouring it back into, the second chamber. Finally, the second chamber was frozen in liquid nitrogen, thus drying the solid in the third chamber. The third chamber was opened and the solid product was bottled under dry helium. The visible and infrared spectra agreed well with those in the literature.¹²

Charge-Transfer Spectroscopy.—The reactants were manipulated under vacuum in the apparatus shown in Figure 1. The solvent reservoir (C), containing a known amount of solvent, was degassed on the vacuum line and attached to the cell chamber (A) above the break seal. The assembly of calibrated pyridine reservoirs (D) were filled by vacuum distillation from a supply of pyridine kept on the vacuum line over calcium hydride. The side tube attached to A contained a known amount of TCNE. After all components were attached, the apparatus was pumped down, sealed by torch, and removed from the vacuum line. The system was manipulated so as to empty the TCNE into A. Solvent was distilled from C into A *via* the break seal. The absorption spectrum of the TCNE solution was recorded, showing no absorbance above 305 nm. The solution was

(15) We thank Dr. O. W. Webster for advising the use of this solvent in place of chlorobenzene.

(16) We are indebted to Dr. O. W. Webster for helpful and generous discussions on the preparation of this salt. Attempts to prepare the salt by the literature method¹⁴ failed.

poured back into A and frozen. Pyridine was distilled into A from one of the reservoirs D. The spectrum was recorded as soon as the mixture thawed and came to room temperature. The solution was immediately poured back into A and refrozen, and the second stored increment of pyridine was distilled into A. This procedure was repeated several times. The same technique was used for the picolines and lutidines.

A Benesi-Hildebrand plot was made when a well-defined charge-transfer band was observed and when there was little distortion of the early spectrum by reaction-product formation. In two cases (2-picoline and 2,6-lutidine) a well-defined band was not observed. In three cases (4-picoline, 3,4-lutidine, and 3,5-lutidine) only two spectroscopic points could be used because of the accumulation of reaction products by the time of the addition of a third increment of the donor. For this reason the equilibrium constants calculated remain questionable (Table I).

TABLE I
SUMMARY OF DATA FOR COMPLEXES WITH TCNE

Donor	λ_{\max} , nm	Equilibrium constant, l./mol	Extinction coefficient, l./mol cm
Pyridine	342	1.3	2680
4-Picoline	347	1.8	2860
2-Picoline	~340 ^a	<i>b</i>	<i>b</i>
3,5-Lutidine	355	1.8	3120
3,4-Lutidine	353	1.6	3250
2,6-Lutidine	<i>c</i>

^a Band was very poorly defined. ^b No attempt was made to determine these values. ^c No charge-transfer band could be detected.

Results and Discussion

Initially, reactions were carried out with a 10-mm path-length cell requiring small concentrations of pyridine and TCNE. At these concentrations, the optical spectra showed only the doublet at 399 and 418 nm characteristic of the pentacyanopropenide ion and a band at 300 nm attributable to the tricyanoethenolate ion. We assume that we were unable to remove the small amount of water necessary for the formation of these ions at the concentrations in question.

A cell with a path length of 0.1 mm permitted the use of concentrations of reactants far higher than that expected of unremoved water, and this enabled the observation of what we consider to be the charge-transfer bands without interference by reaction products. Increments of donor did have to be added rapidly, however, since absorbances owing to reaction products began to distort the charge-transfer bands after *ca.* 30 min. In most cases, the spectrum taken after the third addition of donor showed significant absorbance owing to reaction-product formation and a decrease in the intensity of the charge-transfer band.

No charge-transfer band was detected with 2,6-lutidine as donor, and only weak absorbance with no well-defined maximum could be observed in the 2-picoline-TCNE system. The other four donors, pyridine, 4-picoline, 3,4-lutidine, and 3,5-lutidine, gave broad bands at 340-355 nm. These bands increased in intensity as the donor concentration was increased. The intensity of the bands decreased with time and increasing reaction-product formation. For this reason, spectra taken after addition of the third increment of donor showed lower intensities for the charge-transfer band than were expected. In some cases the intensity of the band after the third increment was lower than that after the second increment.

Benesi-Hildebrand plots were made on absorbance data obtained from these complexes whenever a well-

defined charge-transfer band was observed and whenever there was little distortion of the spectrum owing to reaction-product formation. Only absorbance data from the first two increments of donor could be used because significant amounts of reaction product had accumulated by the time the third addition of donor was made. Considering these limitations, the equilibrium constants obtained are questionable. Results for the complexes are given in Table I.

Although valid comparisons cannot be made from the equilibrium constants, some qualitative differences are evident from the optical spectra. There certainly appears to be some hindrance to complex formation by methyl substitution in the positions adjacent to the nitrogen atom, and the effect is more pronounced with disubstitution than with monosubstitution. Also, if the assumption is made that all of the complexes have approximately equal extinction coefficients, the amount of complexation may be estimated from the intensity of the charge-transfer band after the initial addition of donor, since the concentrations of reactants were the same for each system. The initial spectrum was used, since only small amounts of reaction products had distorted the spectrum and consumed TCNE at this point. The peaks decreased in intensity in the order 3,4-lutidine > 3,5-lutidine > 4-picoline > pyridine. Using this method of analysis, the intensities

of the complex bands of the donors which are not sterically hindered parallel closely their basicities. Although comparisons of the steric effect and order of donor strength are not conclusive, these data indicate that the donors act as n -electron donors toward TCNE.

Esr investigations of the TCNE-pyridine systems showed the nine-line spectrum of the TCNE anion radical, but no evidence was found for any other paramagnetic species. The lack of evidence for the presence of the pyridine cation radical implies that the formation of the TCNE anion radical may not be due to the dissociation of the charge-transfer complex.

The radical anion is formed in good yields by the reaction of TCNE with cyanide ion,¹⁴ and this method was used to synthesize the potassium salt of the anion radical in this laboratory. Since the formation of both pentacyanopropenide and tricyanoethenolate ions in the donor-TCNE systems liberates cyanide ion, this ion is very likely responsible for the reduction of TCNE to the anion radical. This possibility is supported by our finding that the concentration of radical increased slowly over a period of hours.

Registry No.—TCNE, 670-54-2; pyridine, 110-86-1; 4-picoline, 108-89-4; 3,4-lutidine, 583-58-4; 3,5-lutidine, 591-22-0.

Deuterium Isotope Effects in the Principal Electronic Transition of Nitrobenzene and Aniline and Their *p*-Alkyl Derivatives

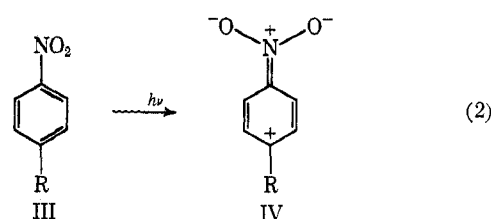
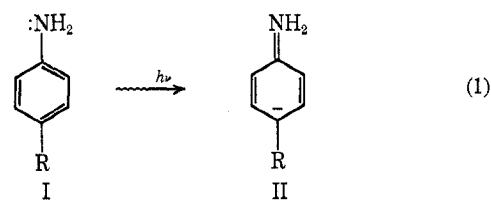
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A study has been made of the effect of *p*-D vs. *p*-H, *p*-CD₃ vs. *p*-CH₃, and *p*-CH₂C(CD₃)₃ and *p*-CD₂C(CH₃)₃ vs. *p*-CH₂C(CH₃)₃ on the principal electronic transition of nitrobenzene and aniline in the gas phase and in heptane solvent. In all but one instance, that of *p*-neopentylnitrobenzene vs. *p*-neopentylnitrobenzene- γ -d₉, deuterium substitution shifted the principal band to slightly higher energies. These results are consistent with the polarizability-electronegativity treatment of substituent effects.

It has been reported that *p*-alkyl substituents substantially lower the energy of the "principal" electronic transition of compounds of the type aniline, phenol, and anisole, the excitation energy order in the gas phase and in heptane being neopentyl (neop) < *t*-Bu, Me < H.¹ It is known that in the principal electronic transition of *p*-disubstituted benzenes (also known as the E band or K band), there is a migration of electronic charge in the long axis of the molecule.² For *para*-substituted anilines, phenols, and anisoles it has been amply demonstrated by solvent studies that the electron migration takes the expected direction, *i.e.*, away from the heteroatom substituent, toward the *para* substituent.³⁻⁵ Thus it may be symbolized by eq 1, in which the formulas I and II are understood to be only approximately representative of ground and



excited states.^{6,7} To anyone holding the static viewpoint that alkyl substituents invariably should act as if electron releasing relative to hydrogen, these results are

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