

REACTIONS OF TETRACYANOETHYLENE WITH SUBSTITUTED PYRIDINES

by

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CHAPTER I

INTRODUCTION

Charge-transfer complexes have been known since the observation that Iodine formed solutions in aromatic solvents which were a different color from those in non-aromatic solvents. The discovery that the color was due to a charge-transfer electronic transition prompted the use of the name charge-transfer complexes.

Recently, many workers have questioned this name, stating that it implies that charge-transfer contributions represent most of the binding energy in the complex. Theoretical arguments show that charge-transfer interactions contribute only slightly to the binding energy in the ground state complex, if at all. Thus the names molecular complex, π -complex, and donor-acceptor complex have been used to describe this association.

In this thesis, these interactions are termed charge-transfer complexes simply because they show a charge-transfer transition in their optical spectra. This name is not meant to imply anything about the relative contribution of charge transfer to the binding energy in the ground state of the complex.

Literature Survey

Since the initial publication of the synthesis and properties of tetracyanoethylene (TCNE) by Cairns and his co-worker in 1958 (1),

a tremendous amount of work has been reported utilizing the unique characteristics of this compound. Due to the electron-withdrawing effect of the four cyano groups, the C-C double bond in TONE is somewhat electron deficient as evidenced by the long C-C bond length (2). This electron deficiency makes TONE a very strong electron acceptor. Tetracyanoethylene enters readily into electron-donor-acceptor-type complexes with virtually all types of electron donors.

Theoretical Considerations

Electron-donor-acceptor complexes, or charge-transfer complexes, are associations of donor (electron-rich) molecules with acceptor (electron-deficient) molecules which exhibit an absorption of ultraviolet or visible light energy not present in either component. This absorption corresponds to an electronic transition in which electron density is transferred from the donor to the acceptor molecule.

Mulliken was the first to treat these molecular complexes quantum mechanically (3). He postulated that the wave function of the complex could be represented as a combination of a "no-bond"-type resonance structure, $|i\rangle(D,A)$, consisting of van der Waals forces and a dative resonance structure, $|i\rangle(D^+-A^-)$, corresponding to electron transfer from the donor to the acceptor. The wave function for the ground-state complex then becomes :

$$|l\rangle_n = a |i\rangle(D,A) + b |i\rangle(D^+-A^-)$$

where $a^2 \gg b^2$ for weak complexes. The excited-state wave function is:

$$|l\rangle_e = a |i\rangle(D^+-A^-) + b |i\rangle(D,A)$$

where $a^* = a$, $b^* = b$ and $a^2 \gg b^2$. The charge-transfer absorption is then due to the $4n^* \rightarrow 4e^*$ transition. Mulliken felt that as the strength of the complex increased, the contribution of charge-transfer forces in the ground state increased. This idea implies that in the interaction of a donor with a low ionization potential and an acceptor with a high electron affinity, the complex in a suitable solvent could exist primarily as ion-pairs, or even as the radical ions.

Dewar and Thompson (4) felt that most chemists misconstrued Mulliken's treatment to mean, that charge-transfer forces were the predominant binding forces in the complex. Dewar argued that the presence of a charge-transfer absorption does not demonstrate anything about the binding energy in the complex. The only requirement for a charge-transfer transition to occur is that the species be close together. The transition could occur equally well if the components were held together by simple van der Waals forces. Mulliken referred to such complexes as "contact" charge transfer complexes (5). The idea of very little charge transfer in the ground state gains support from the low heats of formation of these complexes (6).

In 1949, Benesi and Hildebrand (7) developed a spectrophotometric method for determining the equilibrium constant (K) and the extinction coefficient (e) of the complex. This method or some modification of it has been used by most workers ever since. There has recently, however, been some question as to the validity of this method since the equilibrium constants obtained are dependent upon concentration and wavelength (4).

The complexes of TONE with aromatic hydrocarbons have been exten-

slvely studied in solution (8,9) and also in the gas phase (10) and the solid phase (11). The stability of the complexes of these donors **with** TCNE have been correlated with ionization potentials, steric effects, transannular effects, molecular orbital calculations and solvent effects, among others. These types of complexes will not be covered further in this survey.

Complexes with Heteroatomic Donors

In comparison, little work has been done on complexes of TCNE with heteroaromatic and n-electron donors. Presumably, this is because in many cases subsequent reactions occur which make complex detection somewhat difficult.

In 1962, Liptay, Briegleb and Schindler (12) carried out an extensive study of the $2i \rightarrow |i\rangle |i\rangle |i\rangle |i\rangle$, N-tetramethyl-p-phenylenediamine (TMPD)-TCNE system in solvents of varying dielectric constant. In a solvent of low dielectric constant (diethyl ether) they observed two maxima at **426** and 962 m μ which the authors attributed to the charge-transfer complex. In a solvent of high dielectric constant (acetonitrile), no absorbance was detected in the above region. Instead, only the bands characteristic of the TMPD cation radical and the TCNE anion radical were found. Only at very high concentrations of initial TMPD and TCNE could the complex be detected in acetonitrile. In solvents of intermediate dielectric constant, both the complex and the radical ions could be observed simultaneously.

These results imply that in solvents capable of readily solvating charged species, the complex dissociated into the radical ions. The authors calculated the equilibrium constant not only for complex for-

nation but also for the dissociation of the complex into the radical ions. In acetonitrile, they found that the absorbance due to the TCNE anion radical decreased with time and the absorbance due to the resulting 1,1,2,3,3,-pentacyanopropenide ion increased. In all of the solutions, the Initial absorbances changed with time, and extrapolations to zero time had to be made to determine the equilibrium constants.

Later In 1962, Briegleb, Liptay and Pick (13) published results of the Interaction of TCNE with Br⁻, I⁻, SCN⁻ and (CN)⁻ ions. Addition of Br⁻ to an acetonitrile solution of TCNE gave a complex band at 460 mμ. The spectrum, however, showed rapidly increasing absorbance at 297 mμ and a doublet at 395 and 415 mμ corresponding to the tricyanoethenolate ion, (CN)₃C=C(CN)⁻, and the pentacyanopropenide Ion, respectively.

Interaction with I⁻ gave almost immediately the optical spectrum of the TCNE anion radical and the I⁻ ion. This corresponds to a complete electron transfer from I⁻ to TCNE. At -40 °C, however, a band at 633 mμ attributed to the complex could be observed for one minute. The reaction with SCN⁻ ion gave a red complex which only slowly disappeared to form the tricyanoethenolate ion and the TCNE radical anion in small amounts. Reaction with (CN)⁻ ion gave a stable complex absorbing at 465 mμ which after several hours gave rise to the tricyanoethenolate and pentacyanopropenide ions.

Stamdres and Turkevich (14) found that the interaction of triphenylamine in solution with iodine, trinitrobenzene, or tetracyanoethylene gave colored complexes. These systems also all produced a five-line electron spin resonance spectrum attributed to the triphenyl-

amine-dimer radical cation. No spectrum corresponding to the acceptor radical anion was found. In contrast, when these authors treated triethylenediamine with TCNE, only the esr spectrum of the TCNE anion radical was observed.

Rappoport (15) has studied systems of aromatic amines with TCNE. When *N,N*-dimethylaniline was mixed with a chloroform solution of TCNE, a blue complex was formed with an absorption maximum at 675 m μ . The intensity of this band decreased with time due to a subsequent reaction to form 4-tricyanovinyl-*N,N*-dimethylaniline.

Farrell and Newton (16) studied the same type of system. In the *N,N*-diethylaniline-TCNE system in chloroform or ethylacetate, no significant amount of the 4-tricyanovinyl compound was formed. Their spectrophotometric and esr investigations did, however, show the charge-transfer band at 835 m μ which rapidly disappeared to form the TCNE anion radical and the pentacyanopropenide ion. Similar results were obtained with higher dialkyl anilines and *N,N*-diethyl-*p*-toluidine which cannot undergo substitution in the 4-position.

Isaacs (17) studied the interaction of TCNE with forty-two aromatic amines. The charge-transfer transition energies had a general correlation with the base strengths of the amines. There seemed to be no steric effect from ortho-substituents or from substitution on the nitrogen atom.

Isaacs confirmed the presence of the TCNE anion radical in these systems by esr and visible spectroscopy. He attributed its formation to the dissociation of the complex although the corresponding aniline cation radical was not detected. The absence was attributed to the in-

stability of this species. In acetone, a more polar solvent than that employed by Rappoport, even dimethylaniline gave rise to the TCNE anion radical.

Farrell and Newton (18) used this type of system to determine the ionization potential of aromatic amines, employing the linear relationship between the charge-transfer transition energy and the ionization potential of the donor. They found that alkyl substitution on the nitrogen atom appreciably lowered the ionization potential of the amine. The drop in ionization potential corresponded to increased reactivity, and a considerable amount of pentacyanopropenide ion was formed in the higher N[^]-alkyl-substituted aniline-TCNE systems.

Bonner and Woolsey (19) have recently studied systems of TCNE with a series of amides. Results from their investigation indicate that these amides are n-electron donors in which complex formation occurs through the carbonyl oxygen.

Foster and Goldstein (20) have investigated some arylketone-TCNE complexes and have concluded that these are of TT character. The I₂ complexes with these donors, however, are of an n nature.

The TCNE complexes of phenothiazine and related compounds were studied by Foster and Hanson (21). The charge-transfer band for the phenothiazine-TCNE system occurred at 854 mμ, and for thianthrene, a doublet occurred at 478 and 610 mμ. No side reactions seemed to occur in these heterocyclic systems.

Alkylpyrroles gave charge-transfer bands with TCNE whose intensity decreased rapidly with time as the tricyanovinyl reaction products were formed (22). With 3-methylpyrrole, several other sharp peaks were

present in the optical spectrum indicating the presence of at least three species in addition to the initial reactants.

Cooper, Crowne and Farrell (23) also studied the interaction of TCNE with pyrrole as well as several other five-membered heterocycles. They found weak complexes with pyrrole, thiophene, furan and indole. The nitrogen-containing heterocycles had charge-transfer bands which decreased in intensity as the reaction products formed. Correlations of charge-transfer transition energies with molecular orbital calculations indicated that these heterocycles act as π donors toward TCNE.

Keys and Carper (24) observed an ESR signal when TCNE was dissolved in dimethoxyethane or certain nitrogen and phosphorus-containing solvents such as N,N -dimethylacetamide and hexamethylphosphoramide. The ultra-violet and visible spectra showed absorbances at approximately 300 and 400 m μ which were time-dependent. These reactions, however, were not investigated further.

Stewart and Eisner have studied the interaction of TCNE with dimethylsulfoxide (25) and with dimethylacetamide, acetone and tetrahydrofuran (2,6). In these systems they observed the ESR spectrum of the TCNE radical anion as well as the charge-transfer absorption band at 372 m μ . They attributed the ion formation to the dissociation of the complex. The absence of the corresponding cation radical was attributed to broadening of the ESR signal by the large concentration of donor. Other absorption bands appeared in the DMSO-TCNE system at higher temperatures. These were ascribed to the complex formation of TCNE with sulfite ion and sulfide ion, presumably the decomposition products of DMSO. Addition of Na₂S to an acetone solution of TCNE

gave bands at 400 and 420 mμ and no esr signal.

Stewart and Eisner also obtained esr signals using the other donors studied, with the exception of tetrahydrofuran. This fact correlated well with their conclusion that the THF-TCNE complex was the weakest. Photo-induced esr signals could be generated in all four donor systems with TCNE.

Butler, Oakes and Symons (27) reinvestigated the DMSO-TCNE system in 1968. They did not observe the reported charge-transfer band at 372 mμ, but did observe two bands at 398 and 416 mμ. They felt that the formation of the anion radical was the result of a chemical reaction and was not due to the dissociation of the complex.

By dissolving the TCNE in DMSO and diluting with CCl₄, Butler, et al. obtained the esr signal and the doublet visible spectrum described above. However, when they dissolved DMSO in CCl₄ and added TCNE, no esr signal was observed, and the optical spectrum showed only the band at 372 mμ reported by Stewart and Eisner. Butler, Oakes and Symons concluded from these data that the formation of the TCNE radical anion was associated with the decomposition of the DMSO.

To identify the species responsible for the radical formation, Na²S was added to a THF-solution of TCNE. An esr signal was observed, and the optical spectrum* showed the doublet at 398 and 416 mμ. Butler and co-workers concluded that sulfide ion was the decomposition product of DMSO which reduced the TCNE and that the doublet absorbance was due to complexes of TCNE with sulfide ion.

Complexes with Pyridine

Pyridine occupies an interesting position among the heteroatomic

compounds, in that it is a simple compound which can potentially act [^] as either an n- or a π-electron donor. Higasi, Omura and Baba (28) reported that methyl substitution on pyridine has little effect on the ionization potential, compared with the benzene series; hence, the first ionization potential of pyridine must pertain to the loss of an electron from the nitrogen lone pair. Also Nakajima and Pullman (29) found that the ionization potentials for a number of nitrogen heterocyclic compounds parallel their basicities.

Comparing the Rydberg series measurements of pyridine to those of benzene, El-Sayed, Kasha and Tanaka (30) reassigned the lowest ionization potential of pyridine to a π electron. Recently El-Bayoum J. and Khalil (31) have used the charge-transfer transition energies of a series of nitrogen heterocycles with I₂ as an n-type complex and chloranil as a π-type complex to determine the n- and π-ionization potentials of acridine. They concluded that the n-electron ionization potential was 2.2 eV above that for the π-electron ionization potential.

The complexes of pyridine and substituted pyridines with I₂ and iodine halides have been shown fairly conclusively to be of an n-donation type. Popov and Rygg (32) found that the relative stabilities of the complexes of I₂⁻, IBr and ICl varied in the order: 2-picoline > pyridine > 2,6-lutidine. The anomalous stability of the 2,6-lutidine was explained by steric shielding of the nitrogen atom by the methyl groups. Krishna and Bhowmik (33) observed similar results in that 4-picoline forms a much more stable complex with I₂⁻ than does 2-picoline.

Recently, Mulliken (34) presented some theoretical considerations

of the pyridine-I- charge-transfer complex. In the solid complex the geometry has been shown to be linear, with the I lying along the symmetry axis of the pyridine molecule. The stability of the complex was attributed to the n-donor action of the nitrogen atom.

However, Mulliken feels that although the stability arises from a dative structure formed by removing a lone-pair electron from pyridine, the high intensity of the charge-transfer transition band is possibly due to contributions from a π orbital of pyridine. This theory can also account for the asymmetry of the band which exhibits a bulge on the low-frequency side.

The complex of TCNE with pyridine was first investigated by Merrifield and Phillips (6) along with a series of 22 aromatic hydrocarbons. The pyridine-TCNE system absorbed at 400 and 421.5 m μ , and a Benesi-Hildebrand-type determination gave a value of 12 for the equilibrium constant. This is appreciably higher than the value of 2.0 obtained by these authors for the benzene-TCNE complex.

Simultaneously, Middleton and co-workers (35) published their results for the interaction of TCNE with aqueous pyridine. They observed a chemical reaction which produced pyridinium 1,1,2,3,3-pentacyanopropenide in 81% yield. The reaction was not unique to pyridine, and a general basic hydrolysis of TCNE produced similar salts with several bases studied. Hydrolysis in neutral or acidic solutions, however, produced only tricyanoethenol which was isolated as the tetramethylammonium, N⁺-methylquinolinium, and silver salts.

The optical spectrum of pyridinium pentacyanopropenide in water showed a doublet at 393 (e = 22,600) and 412 m μ (e = 22,100) (35).

The tricyanoethenolate Ion exhibited a single absorption at 397 my
($\epsilon - 11,300$) (36).

In 1964, Nepras and Zahradnik (37) published the results of their investigation of TCNE complexes with nitrogen heterocyclic aromatic donors in chloroform. Their series included pyridine, quinoline, acridine and various 3- and 4-ring nitrogen heterocyclic aromatic donors.

They reported the necessity of having to use fast scanning speeds in several instances where chemical reactions occurred. In some cases, however, the reaction was so rapid that the complex could not be studied. They found that TCNE and pyridine gave a yellow coloration which had been erroneously ascribed by Merrifield and Phillips (6) to **the** charge-transfer complex. They differentiated between a complex and a reaction product by the dependence of the absorption upon dilution (the complex does not obey Beer's law) and band shape. They did not investigate the reaction product further, and no complex was reported for pyridine. The charge-transfer bands for quinoline and acridine, however, were reported at 454 and 549 my, respectively.

In 1965, Nicolau and Cailly (38) undertook an esr investigation of the pyridine-TCNE system in benzene. Their report contains no information concerning the purification of reagents or solvents.

In their pyridine-TCNE system, in which the concentration ratio of pyridine to TCNE was 1:9, a slightly unsymmetrical esr singlet was obtained. If the ratio were changed to 2:8, nine hyperfine lines were observed superimposed on what appeared to be a base line resembling one broad singlet. The authors assigned the singlet to the pyridine-TCNE complex, presumably a triplet. The spectrum with the hyperfine structure

was attributed to the simultaneous observation of the complex and TCNE radical anion spectra superimposed. If the concentration ratio were made 5:5, only the nine-line hyperfine spectrum was observed with no singlet distortion. They remarked that both the complex spectrum and the TCNE radical anion spectrum show exactly the same g-value.

With a concentration ratio of pyridine to TCNE of 1:2, a temperature dependence of the esr spectrum was noted. At 293°K only the singlet was present. At about 250°K unresolved hyperfine lines began to appear. At 223 K hyperfine lines were superimposed on a singlet baseline and at 208 K only the nine-line spectrum of the TCNE anion radical was observed.

In subsequent experiments, optical spectra were recorded for the singlet and singlet-hyperfine systems. In the first system, an absorbance was recorded at 400 m μ with a band width of 1017 cm⁻¹. The second system gave a doublet at 402 and 420 m μ with a band width of 431 cm⁻¹.

From their data, the authors concluded that the temperature dependence of the TCNE anion radical shows the exothermic nature of the reaction which gives rise to its formation. No account was given of the fate of the pyridine cation radical which would arise from the proposed dissociation of the charge-transfer complex to produce the TCNE anion radical. Also no explanation was given for the increase in concentration of the TCNE anion radical with respect to the paramagnetic complex species as the concentration ratio was changed.

Later, Pen'kovskii (39) published work on the interaction of TCNE with neat pyridine and its methyl derivatives. He observed that when

TCNE was dissolved in pyridine, 2,4-lutidine, or 2,6-lutidine under vacuum, an Intense esr spectrum was produced. When stored at room temperature, a gradual reduction of the signal was noted. The esr spectrum consisted of nine lines, in agreement with previously published data for the TCNE anion radical (40).

Pen'kovskii ascribed the presence of the TCNE anion radical to acceptance of an electron from the lone-pair on the pyridine nitrogen atom. He implied that the pyridine cation radical then underwent secondary reactions and was not detectable.

In 1967, Farcasiu and Nicolau (41) carried out a study of the molecular complexes between TCNE and substituted pyridines in chloroform. A portion of their data is reproduced in Table I:

TABLE I

Charge-Transfer Data Reported
by Farcasiu and Nicolau

Pyridine Derivative	K^a	X_{\max} (my) ^b
pyridine	10(12) ^c	.400
2-picoline'	13.7	400
3-picoline	72	400
4-picoline	(109)	400
2,6-lutidine	1.06	400
2,4,6-collidine	90	400

a Units cannot be inferred from the authors' data

b For the stronger peak of a doublet

c Reference 6

d The actual value must be higher (close to 850), see below.

They compared the values:

$$\log [K(2,4,6\text{-picoline})/K(2,6\text{-lutidine})] = 1.929 \text{ and}$$

$$\log [K(4\text{-picoline})/K(\text{pyridine})] = 1.038..$$

Since the methyl group in the 4-position should have only an electronic effect, the second ratio should equal the first. They concluded, therefore, that the actual K value **for** 4-picoline should be 850.

The authors noted a pronounced steric effect in the 2- and 6-positions of pyridine with respect to complex formation with TCNE. As expected, the electron-releasing effect of the methyl groups stabilized the complex. It is interesting to note that they found **complex formation** to be a slow process and took readings four hours after mixing. **From** the steric effect, they concluded that pyridine must form either an n complex or a localized π complex with the TCNE molecule very near **the** nitrogen atom.

Recently, Ilten, Kronenberg and Calvin (42), in a search for organic systems which would give reversible esr photosignals, studied the TCNE-pyridine system. They found that TCNE dissolved in neat pyridine gave a dark brown solution and a nine-line esr signal in the dark. Also, a solution of 0.05 M pyridine and 0.5 M TCNE in dichloroethane exhibited the same spectrum. . This system was not further examined.

Studies of the Tetracyanoethylene Anion Radical

Due to the high electron affinity of TCNE, estimated to be on the order of 150 kcal./mole (43), the compound is easily reduced to the anion radical.

Phillips, Rowell and Weissman (40) found that in addition to the common reductions with active metals, TCNE undergoes reduction in tetrahydrofuran or acetonitrile solutions by reaction with I^- or SCN^- ions. They found that when solutions of TCNE and I^- or SCN^- are mixed, a purple color forms which changes to yellow in about five minutes. The purple color was attributed to the charge-transfer complex between TCNE and the anions. The yellow solution was reported to have a maximum absorbance at 432 m μ .

The esr spectrum showed eleven lines with a splitting of 1.56 ± 0.02 gauss ($g = 2.0026 \pm 0.0002$). The central nine lines gave intensity ratios of 1:4:10:16:19:16:10:4:1 expected for interaction with four equivalent nitrogen nuclei ($I = 1$). They found that the end lines were naturally-occurring C^{13} splittings in the CN groups.

Almost simultaneously, Webster, Mahler and Benson (44) published preliminary results of a similar study. They also found reaction with KI to be a convenient laboratory synthesis of the TCNE anion radical. The radical in the solid state was stable to atmospheric conditions and moderate temperatures. In solution, however, the radical was very sensitive to oxygen and, to a lesser degree, to water. Reaction of the TCNE anion radical with water gave a 76% yield of the tricyanoethenolate ion. The action of dilute hydrochloric acid on the radical produced an equimolar mixture of TCNE and tetracyanoethane.

A polarographic study of TCNE and its derivatives was undertaken in 1961 by Rieger, Bernal and Fraenkel (45). These authors found that the anion radical was produced by simply dissolving TCNE in N,N-dimethylformamide. In acetonitrile, the TCNE was reduced electrolytically to

give an esr spectrum which was identical to that previously reported for the anion radical (40). Electrolytic reduction of 1,1,2,2-tetracyanocyclopropane gave a similar esr spectrum except that the line widths were much smaller in the latter system. This was ascribed to the absence of any neutral TCNE molecules in the second system which would cause exchange broadening. The excellent resolution afforded by the narrow lines allowed the observation of 20 lines attributable to the ^{13}C splittings. The cyano ^{13}C splitting was assigned a value of $9.54 \pm .01$ gauss and the ethylenic ^{13}C splitting, a value of $2.20 \pm .01$ gauss.

In 1962, Webster, Mahler and Benson (46), published a comprehensive study of the TCNE anion radical. Most importantly, they observed the formation of the radical by reaction of TCNE with CN^- in acetonitrile. They could not detect the presence of cyanogen in their system; however, added cyanogen could not be recovered.

The authors also reported that tertiary aliphatic amines reacted with TCNE to form the corresponding ammonium tetracyanoethylene. They remarked that the source of the proton was not known. Webster, et al. found that when oxygen was bubbled into an acetonitrile solution of the radical anion, pentacyanopropenide and tricyanoethenolate ions were produced in 36 and 22% yields, respectively.

The infrared spectrum of the anion radical obtained by Webster and his co-workers showed absorption at 4.53, 4.58 and 7.33 μ . The optical spectrum of an acetonitrile solution of the radical showed a broad band with numerous vibrational hyperfine maxima: 468(f. = 4400), 457(5670), 445(6520), 435(7100), 425(7100), 416(6890), 407(6200),

390(4660), 382(3810), 374(3070), and 366 mμ(2440).

Fornal and co-workers (47) observed that OH⁻ ions would also reduce TCNE to the anion radical. They found the esr spectrum of the radical even in mixtures of TCNE in neutral 1:1 distilled water-ethanol solutions. The appearance of the anion radical was accompanied by a drop in pH of the solution. To further confirm their findings, hydrogen peroxide was detected in these systems.

Statement of the Problem

It appears that in light of Middleton's observation that pentacyanopropenide was formed in the reaction of TCNE with aqueous pyridine and that this ion absorbed at 393 and 412 mμ (35), the reported complexes of pyridine and TCNE (6,41) were probably only an observation of this ion formation. Assuming this to be true, the charge-transfer spectrum of the TCNE-pyridine system has never been observed.

The problem then was to detect this complex, and if successful, to use methyl-substituted pyridines as donors to gain insight into the type of complex formed. If a ππ complex were formed, methyl substitution in any position should stabilize the complex. If an n complex were formed, the electronic effect of methyl substitution would again stabilize the complex, however, the steric effect of a methyl group in the 2- or 6-position should markedly decrease the stability of the complex with TCNE.

In an attempt to find the source of the TCNE anion radical, an investigation of the reduction of TCNE was also undertaken.

CHAPTER II

EXPERIMENTAL

Purification of Reagents

Tetracyanoethylene

Tetracyanoethylene was purified by a modification of the literature method (48). Five grams of commercial tetracyanoethylene (Aldrich Chemical Co., Inc., Milwaukee, Wisconsin) was dissolved in 75 ml. of hot chlorobenzene. Decolorizing charcoal was added and the hot solution was filtered. The solution was then concentrated to about 50 ml. by passing a stream of nitrogen gas over the boiling solution. Upon cooling undisturbed, large, delicate yellow crystals formed. These crystals were filtered, washed with a little cold solvent, and air dried.

Recrystallization from 1,2-dichloroethane as suggested by Webster (49) using the above procedure gave almost colorless crystals. This, coupled with the fact that the lower boiling point of this solvent allows faster evaporation, made this system preferable for purification of TCNE.

The recrystallized product was sublimed at 90 with the use of either an aspirator suction or a small vacuum pump. The aspirator vacuum allowed slower sublimation which produced very fine colorless needles of TCNE. This purified product was stable for months in a screw-cap vial.

Pyridine and Methyl-substituted Pyridines

. Since water was the main interference in our system, the purification procedure for the pyridines consisted mainly of drying techniques. All of the bases were treated in the same manner; therefore, pyridine will be used as an example.

The pyridine (Matheson, A.C.S. Analyzed Reagent Grade; the methyl-pyridines were Aldrich Chemical Co. products) was refluxed for several hours over fresh CaH₂ in a system protected by a CaCl₂ tube. The distilling head could be switched from reflux to distillation by turning a stopcock, and did not, therefore, expose the pyridine to the atmosphere.

The distillate was collected in an Erlenmeyer receiver, containing fresh CaH₂. Only the middle fraction of the pyridine was collected. None of the boiling ranges for the bases exceeded 0.5 and the corrected boiling points agreed favorably with handbook values. The bases were then stored in glass-stoppered or screw-cap vials over CaH₂ until used.

Purification of Solvents

Methylene Chloride

As with pyridine, the predominant consideration in the purification of the solvents used was the exclusion of water. Methylene chloride was refluxed over P₂O₅ for several hours using the previously described reflux distilling head. The middle fraction with a constant boiling range was collected in a receiver containing fresh P₂O₅. The receiver flask was stoppered, with a septum and the solvent was removed with a syringe as needed. Methylene chloride was used exclusively

as **the** solvent in the study of complex formation between TCNE and the substituted pyridines.

Acetone

Acetone was dried according to the procedure of Timmermans and Glllo (50). The acetone was first fractionally distilled through a 30-cm. Vigreux column. The uncorrected boiling range was 53.3-53.6°. Anhydrous CaCl_2 was added and the acetone again fractionally distilled. The partially dried-acetone was treated with P_2O_5 and distilled. The distillate was treated with fresh P_2O_5 and fractionally distilled. The final uncorrected boiling range was 53.4-53.6°. The receiving flask was immediately stoppered with a septum and samples removed with a syringe. Timmermans and Glllo claimed that acetone dried in this manner contained less than 0.001% water.

Acetonitrile

In Initial experiments the acetonitrile (Matheson, Spectre-quality Reagent) was dried by refluxing for several hours over P_2O_5 using a reflux distilling head and distilling onto fresh P_2O_5 . Later experiments were carried out using commercial anhydrous acetonitrile (Eastman Organic Chemicals). This product comes in a septum-stoppered bottle over molecular sieve and has reportedly less than 0.01% water content. This solvent was either used directly from the bottle or was placed in the apparatus over P_2O_5 .

Preparation of Compounds

Pyridinium 1,1,2,3,3-Pentacyanopropenide

Pyridinium 1,1,2,3,3-pentacyanopropenide (PCNP) was prepared by a modification of the procedure given by Middleton, et al. (35). Tetracyanoethylene (1.28 g., 10 mmoles) was dissolved in 10 ml. of acetone and the solution was cooled to -50° . Nitrogen was bubbled through the solution for 15 minutes to displace the oxygen. A solution of 0.395 g. of pyridine (50 mmoles) and one ml. of water was added through a dropping funnel over a period of one minute. The resulting deep purple solution was allowed to warm to room temperature. As warming occurred, the solution became dark brown. The mixture was air evaporated to nearly dryness and the brown residue collected on a filter. The crude product was recrystallized four times from water before a satisfactory melting point of $166.5-168.0$ was obtained; literature value, $167-168^{\circ}$ (35).

To determine whether or not water was required for the formation of pyridinium PCNP, the reaction was carried out in a sealed vacuum system under anhydrous conditions. Also, the reaction was run with methylene chloride as solvent to determine whether the reaction occurred in less polar solvents.

The vacuum apparatus contained 1.28 g. of TCNE in a reaction chamber to which was attached two break-seal reservoirs. One of these reservoirs contained degassed pyridine over CaH_2 , and the other contained degassed methylene chloride over P_2O_5 . Each end of the system was sealed with a break-seal tube, the outer end of which was capped with a septum.

The apparatus was evacuated, flamed and sealed. The solvent was introduced by breaking the break-seal and distilling the CHCl_3 (10 ml.) onto the TCNE with liquid nitrogen. In a similar manner, the pyridine (0.4 ml.) was distilled into the suspension. The solution became very dark and was left at room temperature for 36 hours. No solid could be observed in the dark liquid.

The end break-seals were then broken and helium was passed through the system. The outlet was attached to a gas-washing bottle containing a solution of Ba(OH)_2 to check for the evolution of CO_2 . No precipitate of BaCO_3 could be seen; therefore, it was concluded that little or no CO_2 was produced by the reaction.

The purge was continued until all of the solvent had been evaporated. The reaction tube was then broken under a helium flush and a sample of the dark residue was removed. An infrared spectrum in a KBr pellet showed the product to be TCNE with a small amount of PCNT impurity.

The anhydrous experiment was repeated with acetone as the solvent. The anhydrous acetone (see p.21) was not placed over a drying agent in the break-seal reservoir. In this instance CO_2 was given off. The resulting BaCO_3 was filtered, dried and weighed. The quantity of BaCO_3 obtained corresponds to 0.3 mmole or 6% of the theoretical amount.

The infrared spectrum of the resulting solid shows absorbances characteristic of authentic PCNP. The optical spectrum shows a poorly defined peak at 400 m μ . These data indicate that some PCNP was formed; however, it appears to be very contaminated with other products.

Tetramethylammonium Tricyanoethenolate

Tetramethylammonium tricyanoethenolate was prepared by a modification of the procedure of Middleton, et al. (35). One gram of TCNE was added to 4 ml. of water and refluxed until the TCNE had dissolved. Then 0.85 g. of tetramethylammonium chloride was added to the reaction mixture and the hot solution was filtered. Upon cooling, the product separated as long yellow needles which were filtered and washed with water and ethanol. The product melted at 210° , in good agreement with the cited literature value ($210-211^{\circ}$).

Potassium Tetracyanoethylene

Several attempts were made to prepare this radical anion salt, most of them following the procedure of Webster, Mahler and Benson (46) using CN^{-} ion. The first attempts failed due apparently from failure to exclude oxygen completely. Success was finally obtained by carrying out the reaction of TCNE with CN^{-} in a sealed glass system under vacuum.

Following Webster's suggestions (49), the KCN was recrystallized from a water-ethanol mixture to remove carbonates and dried in a pistol dryer at about 96° (refluxing heptane) for two hours immediately before use. The acetonitrile was Eastman anhydrous (septum-capped) and was transferred via syringe. The vacuum apparatus used consisted of three separate chambers, one of which was separated by a sintered-glass disk from the other two.

Potassium cyanide (2.65 g.) was placed in the first chamber along with molecular sieve (Linde, 3A) and 50 ml. of acetonitrile. Tetra-

cyanoethylene (5.10 g.) was placed in the second chamber. The apparatus was then connected to a high vacuum line and the acetonitrile was degassed by a series of freeze-thaw cycles. The apparatus was then sealed under vacuum with a torch.

The suspension of KCN in acetonitrile was cooled to -5° in an ice-salt bath and was then poured onto the TCNE. A violent bubbling ensued and the solution became very dark. The mixture was stirred for two hours with an enclosed magnetic stirring bar and then filtered through the sintered-glass disk into the third chamber. After standing overnight, a bronze product collected on the walls of the tube. The dark solution was then filtered from this product and clean solvent was distilled back into the third chamber to wash the product. This wash solvent was poured back through the filtering disk and all of the solvent was frozen in the second chamber with liquid nitrogen. The freezing dried the product and the tube was broken while the solvent was frozen. The bronze solid was further dried with a helium purge and the platelets were scraped from the walls. No attempt was made to further purify the product. The infrared and visible spectra agreed with the reported data for the TCNE anion radical (46) (Figure 1).

Apparatus and Procedure

Pyridine-TCNE Charge-Transfer Complex

. Since TCNE readily undergoes basic hydrolysis (35) and the TCNE radical anion reacts with water and oxygen (46), the study of complex formation between TCNE and pyridine (and the methyl-substituted pyridines) had to be carried out in a glass vacuum apparatus using anhydrous, degassed reagents and solvents (See Figure 2).

Figure 1. Optical spectrum of the TCNE anion radical in acetonitrile.

$$[\text{KTCNE}] = 8.0 \times 10^{-4} \text{ M}$$

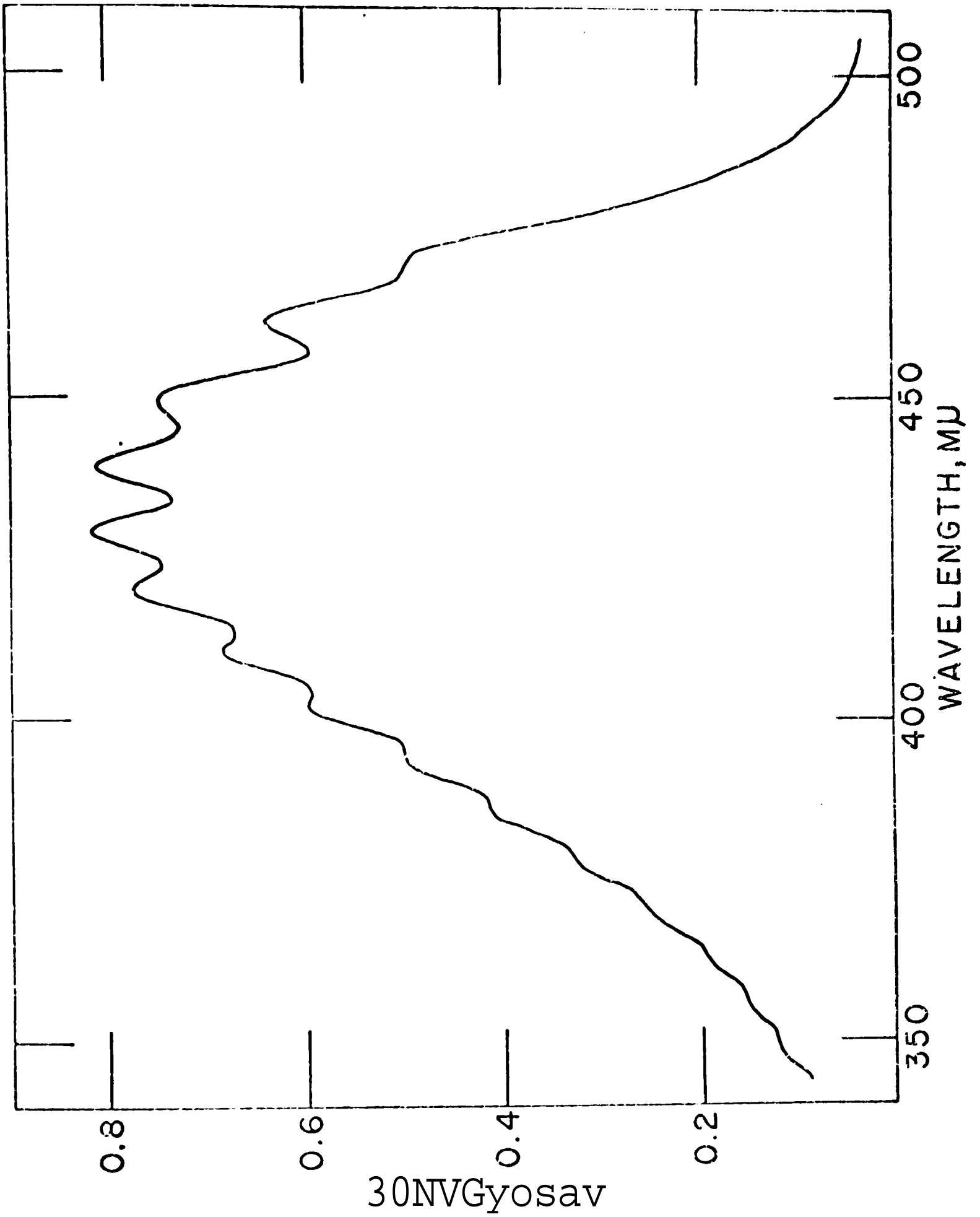
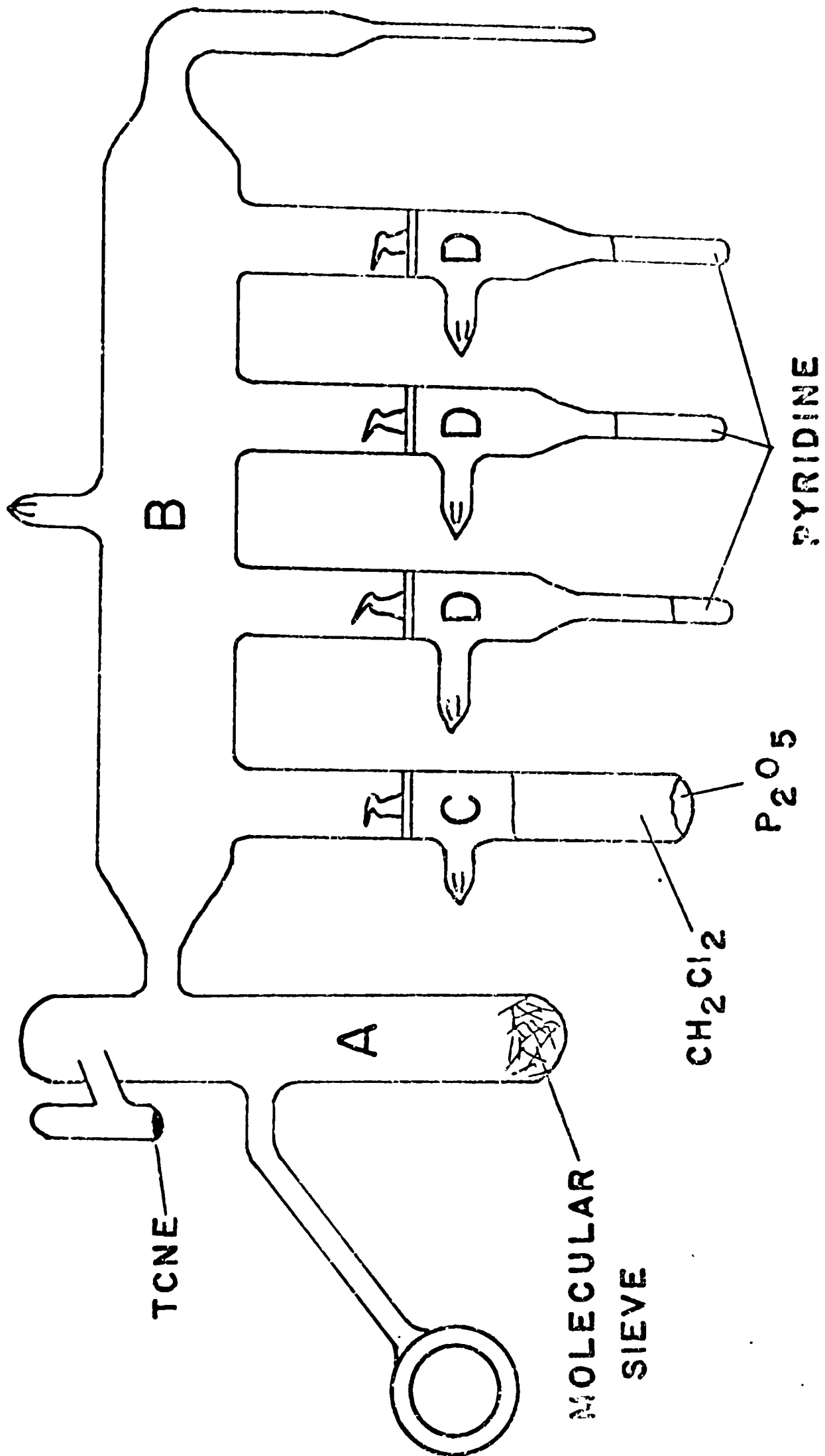


Figure 2. All-glass, break-seal vacuum apparatus used to study charge-transfer complex formation.



The apparatus consisted of a reaction tube (A) to which was attached an optical cell and a small side tube for the TCNE. Also attached to the reaction tube was a manifold (B) with a capillary on the end for esr studies. The manifold had four break-seal reservoirs attached to it which held the dry, degassed solvent and reagent.

The solvent reservoir (C) was prepared by sealing the bottom end of a break-seal tube and attaching to the side a long curved tube ending in a standard-taper joint. A small amount of P 0 was introduced through the side tube into the reservoir. Then 5 ml. of methylene chloride was added with a syringe. The apparatus was then connected to a high-vacuum line (oil-diffusion pump), the solvent frozen in liquid nitrogen, and the system evacuated to 10~ mm. Hg. The solvent was degassed by 3-5 successive freeze-thaw cycles, and the side tube was sealed off with a torch. This reservoir was then attached to the manifold above the break-seal.

The pyridine reservoirs (D) were made by attaching a 4-cm. length of 6 mm. I.D. glass tubing to the bottom of a break-seal tube and sealing the end of this tubing. Another length of tubing was then joined to the side of the reservoir and two 3-mm. lengths of molecular sieve (Linde, 3A) were placed in the reservoir through this tube.

Three such reservoirs were attached by their side tubes to a manifold. Also attached to the manifold were two chambers in series with a stopcock between them and the manifold. In the chamber nearest the manifold was placed molecular sieve. In the other chamber, a small amount of fresh CaH₂ was introduced along with 2-3 ml. of pyridine. The apparatus was then attached to the vacuum line, and the pyridine

was degassed by freeze-thaw cycles. The pyridine was allowed to react with the CaH^{\wedge} until bubbles could no longer be observed. The pyridine was then frozen and the system evacuated while the chamber containing the molecular sieve was warmed with a cool flame to expel any water. After cooling, the pyridine was distilled onto the dried molecular sieve. After standing for a period of time over the molecular sieve, the pyridine was frozen and the system again evacuated. A cool flame was then used to flame the reservoirs and manifold. The system was evacuated for 30 minutes with occasional flaming of the reservoirs to dry the molecular sieve in them.

The 6-mm. I.D. tubing on the bottom of the reservoirs had been calibrated with pyridine in order to get a good estimate of the weight of pyridine in the reservoir. The value of 25.3 mg./mm. for pyridine was multiplied by the appropriate density ratio to obtain calibration factors for the methyl-substituted pyridines.

The desired amount of pyridine could then be distilled from the vacuum chamber into the break-seal reservoirs. The side tubes were then sealed off with a torch and the reservoirs attached to the reaction apparatus manifold.

The procedure for the study of complex formation consisted of placing a small amount of molecular sieve in the reaction tube and sealing this tube. A weighed amount of TCNE was introduced into the side chamber and the top of this chamber was sealed. The apparatus was connected to the high-vacuum line, evacuated, and the entire system flamed with a torch to remove adhering water. The molecular sieve in the reaction tube was also frequently warmed. The TCNE could not be

warmed due to its ready sublimation and was kept slightly cool by occasional exposure to liquid nitrogen for a few seconds. Caution was exercised, however, to allow the TCNE to warm periodically to prevent water from condensing in the chamber. The TCNE side chamber was made very small in order that the minimum amount of surface area would escape flaming.

The apparatus was then removed from the line under high vacuum by sealing with a torch. The system was then manipulated to empty the TCNE into the reaction tube. The solvent break-seal was broken with an enclosed Teflon-coated magnet, and the methylene chloride distilled into the reaction tube by cooling the tube with liquid nitrogen. Upon thawing, the TCNE dissolved in the solvent to form a colorless solution. The optical spectrum was taken of this solution in the region 600-290 m μ . The TCNE absorbance went off scale at 290 m μ ; however, no absorbance could be detected above 305 m μ .

The solution was poured from the optical cell back into the reaction tube and was frozen. The first pyridine break-seal was broken and the pyridine distilled into the reaction tube. As the mixture thawed, the yellow solution was mixed by shaking. The optical spectrum was taken as soon as the system reached approximately room temperature.

Immediately after taking the spectrum, the solution was poured back into the reaction tube and refrozen to prevent any chemical side reactions from proceeding. The second increment of pyridine was introduced in a similar manner and the spectrum again taken. The third increment of pyridine was finally added.

A Benesi-Hildebrand-type plot (See Appendix) was made on the data obtained from these complexes whenever a well-defined charge-transfer

band was observed and whenever there was little distortion of the spectrum due to reaction product formation. In some cases a well-defined **peak** was not obtained (2-picoline and 2,6-lutidine) and in others only two points could be used because of accumulation of reaction products by the time the addition of the third increment of donor was made (4-picoline, 3,5-lutidine and 3,4-lutidine). For this reason, the equilibrium constant values obtained are questionable. The equilibrium constants and the extinction coefficients for these complexes are given in Table II. These values were determined at the wavelength of maximum absorbance.

TABLE II

Summary of Data for Complexes with TCNE

Donor	λ_{max} (m μ)	Equilibrium Constant (l./mole)	Extinction Coefficient (l./mole cm.)
Pyridine	342	1.3	2680
4-Picoline	347	1.8	2860
2-Picoline	340 ^a	b	b
3,5-Lutidine	355	1.8	3120
3,4-Lutidine	353	1.6	3250
2,6-Lutidine			

a Band was very poorly defined.

b No attempt was made to determine these values

c No charge-transfer band could be detected.

For comparison, the pK^{\prime} 's of the donors are given in Table III. The pK^{\prime} 's here correspond to the dissociation of the conjugate acid of the donor.

TABLE III

Basicity Constants for Donors Studied^a

Donor	PC
Pyridine	5.2
4-Picoline	6.0
2-Picoline	5.9
3,5-Lutidine	6.2
3,4-Lutidine	6.5
2,6-Lutidine	6.6

a Reference 51

b Dissociation constant for the conjugate acid of the base

The esr spectra could only be taken after all of the optical measurements had been made since the solutions could not be quantitatively transferred back from the capillary to the reaction tube.

Thianthrene-TCNE Charge-Transfer Complex

The weak basicity of thianthrene allowed its charge-transfer complex with TCNE to be studied without resorting to a vacuum apparatus or an anhydrous solvent. Mixtures of thianthrene and TCNE in CH_2Cl_2

exhibited two charge-transfer maxima in the visible spectrum at 478 and 610 m μ as had been reported (21).

The equilibrium constant for this complex was determined in two ways. In the first, the concentration of TCNE was held constant at 5×10^{-3} M and the concentration of thianthrene was varied from 1.0×10^{-2} to 10.0×10^{-2} M. In the second method, the concentration of thianthrene was held constant at 5×10^{-2} M and the concentration of TCNE was varied from 1.0×10^{-4} to 10.0×10^{-4} M.

A Benesi-Hildebrand treatment of both sets of data gave straight lines for each maximum. In each method an average of the equilibrium constants for each maximum was used as the equilibrium constant for the complex. It is generally accepted that two charge-transfer maxima represent transitions from the highest and second-highest occupied orbitals of the donor and do not represent different types of complexes (52).

The first method gave a K value of 2.0 and an extinction coefficient of 270. The second method gave a K value of 1.4 and an extinction coefficient equal to 415.

CHAPTER III

DISCUSSION AND INTERPRETATION OF RESULTS

TCNE-Pyridine Charge-Transfer Complex

On dissolving TCNE in pyridine, a yellow to caramel-colored solution is formed which exhibits an intense esr signal. This is in agreement with the previously reported observation of Pen'kovskii (39). **The** esr signal (Figure 3) consists of nine major lines with a splitting of 1.54 gauss characteristic of the interaction with four equivalent nitrogen atoms in the TCNE anion radical. Higher signal levels show an additional line at each end of the spectrum with approximately the same splitting constant. These lines are attributed to naturally-occurring

13

C Interactions in the molecule (40). The signal is obtained not only upon dissolving TCNE in neat pyridine, but also upon mixing the two components in CH₃CN or CH₂Cl₂.

The optical spectrum of the TCNE-pyridine system, with pyridine, methylene chloride, acetonitrile or nitromethane as solvent, shows an intense doublet at approximately 400 and 420 mμ. An equally intense absorbance at about 300 mμ appears as a shoulder on the TCNE band. The TCNE absorbance rapidly goes off-scale at 290 mμ.

From the reported observations of Middleton, et al. (35) the doublet appears to be due to the pentacyanopropenide ion. The pyridinium salt of this ion was synthesized and its optical spectrum in CH₂Cl₂ is shown in

Figure 3. Electron spin resonance spectrum of the TCNE anion radical. (Only the seven center lines are shown.) The arrow represents increasing magnetic field and one gauss.

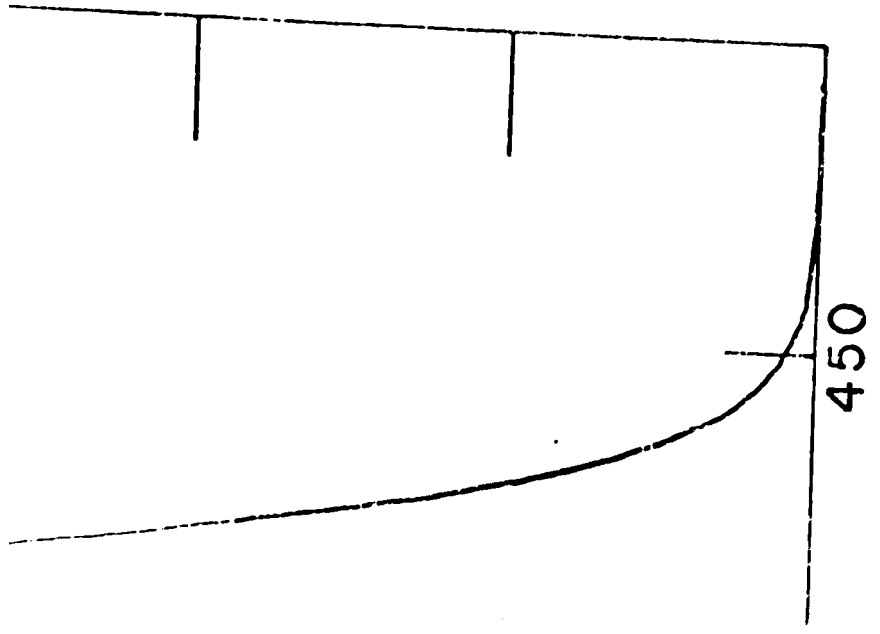
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A

Figure 4. Optical spectrum of pyridinium pentacyanopropenide
in CH₂Cl₂.

[PCNP] = 4.0 X 10⁻⁴ M

r



Λ

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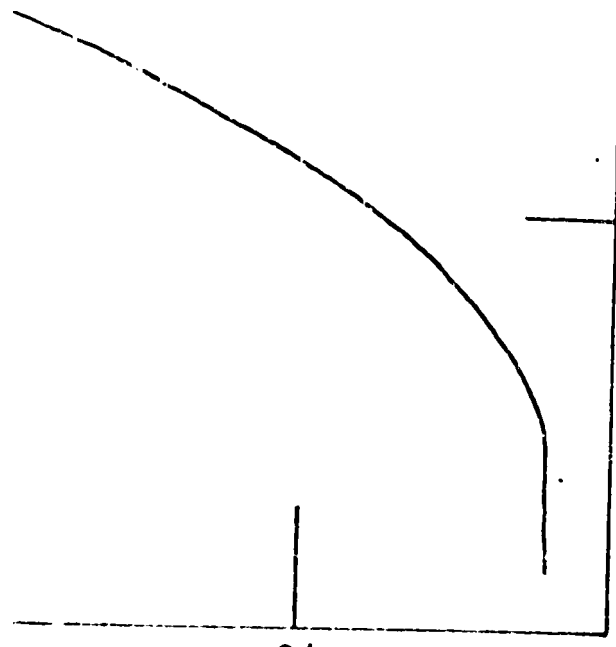
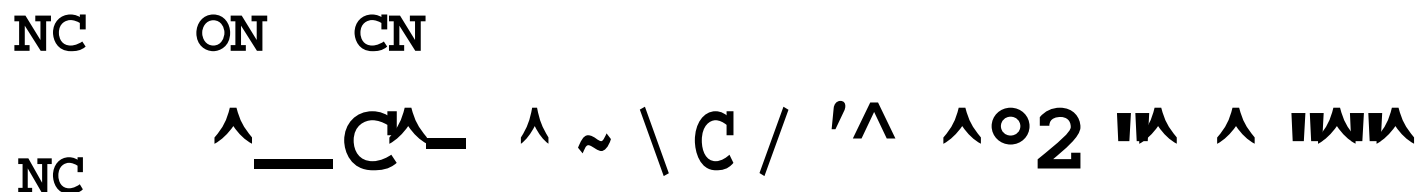


Figure 4. It is immediately apparent that these maxima at 399 and 418 my correspond very closely to the maxima given by Merrifield and Phillips (6) for the charge-transfer bands of the TCNE-pyridine system. The spectrum observed by these authors is very likely due, not to a charge-transfer complex, but to the PCNP ion. Nepras and Zahradnik (37) noted that the yellow color of the TCNE-pyridine system was erroneously ascribed by Merrifield and Phillips to a charge-transfer complex, but Nepras and Zahradnik did not identify the product responsible for the color.

It is interesting in light of these observations to review the study of complex formation between substituted pyridines and TCNE reported by Farcasiu and Nicolau (41). Although their equilibrium constants varied widely (Table I), the charge-transfer maxima were identical in each system. The authors also reported that these maxima represent the more intense peak of a doublet. Apparently they too observed only the formation of PCNP ions and not the charge-transfer complex. This is supported by the fact that Farcasiu and Nicolau found complex formation to be a slow process.

These observations are not surprising since Middleton (35) has shown that TCNE readily undergoes basic hydrolysis to form the PCNP ion:





The 300-m μ peak was found to be due to the tricyanoethenolate ion as **verified** by a spectrum of the synthesized tetramethylammonium salt of this **ion**. This compound is the hydrolysis product of TCNE and the TCNE **anion** radical. The TCNE anion radical also reacts with oxygen to **give both** the PCNP and the tricyanoethenolate ions (46).

The literature on complex formation between TCNE and heteroatomic **donors** becomes somewhat clearer with considerations of the preceding **chemical** reactions. Briegleb and Liptay (12,13) observed the formation of the TCNE radical anion in their interaction of TCNE with tetramethylphenylenediamine and various anions. The anion radical concentration **decreased** with corresponding increases in the concentration of PCNP and tricyanoethenolate ions.

The interaction of TCNE with substituted anilines by Farrell and Newton (16,18) gave PCNP in many cases, especially where it was impossible to form the tricyanovinyl compound. Upon dissolving TCNE in dimethylacetamide and hexamethylphosphoramide, Keys and Carper (24) found absorbances at 300 and 400 m μ which were time dependent. Stewart, et al, (25) observed bands at 400 and 420 m μ when sodium sulfide was added to an acetone solution of TCNE. A reinvestigation of the same system by

Butler, Oakes and Symons (27) showed a doublet at 398 and 416 μ with **THF** as the solvent. Butler, et al. attributed these absorbances to complexes between sulfide ion and TCNE. The authors also obtained the **doublet** upon dissolving TCNE in dimethylsulfoxide. They correlated **these data** by assuming that the sulfide ion was a decomposition product of DMSO. Nicolau and Cailly (38) observed the doublet at 402 and **420** μ in their pyridine-TCNE system, but did not explicitly designate **the** species responsible.

In **each** of the above instances, the TCNE systems contained donors **which** are more or less basic. It is proposed, therefore, that these cases show either the basic hydrolysis of TCNE or the reaction of the TCNE anion radical with oxygen.

The basic hydrolysis studies of Middleton imply that water is required to interact with the pyridine (or other basic molecule) to generate OH⁻ ion which adds to the TCNE double bond. A reasonable mechanism could not be proposed which used the base directly and did not generate OH⁻ ion. This idea is substantiated by attempts* at anhydrous preparations of the PCNP ion. (See p. 22). No PCNP was produced with anhydrous pyridine and CH₂Cl₂ in a vacuum system. Also no CO was given off. Some PCNP was formed with acetone as the solvent and some CO was given off. This could have been due to the fact that acetone is harder to dry and also that the acetone after drying was not stored over a drying agent. In any case, even with acetone as the solvent, **the** PCNP was not formed in good yields under anhydrous conditions.

The logical way, therefore, to study the complex formation between pyridine and TCNE without producing the PCNP or tricyanoethenolate

ions was to use completely anhydrous and deoxygenated conditions. The apparatus shown in Figure 2 was designed for this purpose.

The Initial studies in this system were made using an attached optical cell with a path length of 10 mm. This required typical concentrations of:

$$[\text{TCNE}] = 5 \times 10^{-4} \text{ M}$$

$$[\text{pyridine}] = 0.1 - 0.3 \text{ M}$$

A typical optical spectrum obtained using this apparatus and procedure is shown in Figure 5. The only apparent absorbances were due to the tricyanoethenolate ion at 300 m μ and the pentacyanopropenide ion at 399 and 418 m μ . There was also some weak absorbance at longer wavelengths. These peaks increased in intensity slowly with time and increasing pyridine concentration.

Although only the peaks described above are immediately evident, subtracting the absorbances due to the reaction products, PCNP and tricyanoethenolate ions, shows a broad weak band at about 350 m μ . The absorbances of the reaction products were determined from extinction coefficients calculated from the spectrum of the synthesized compounds.

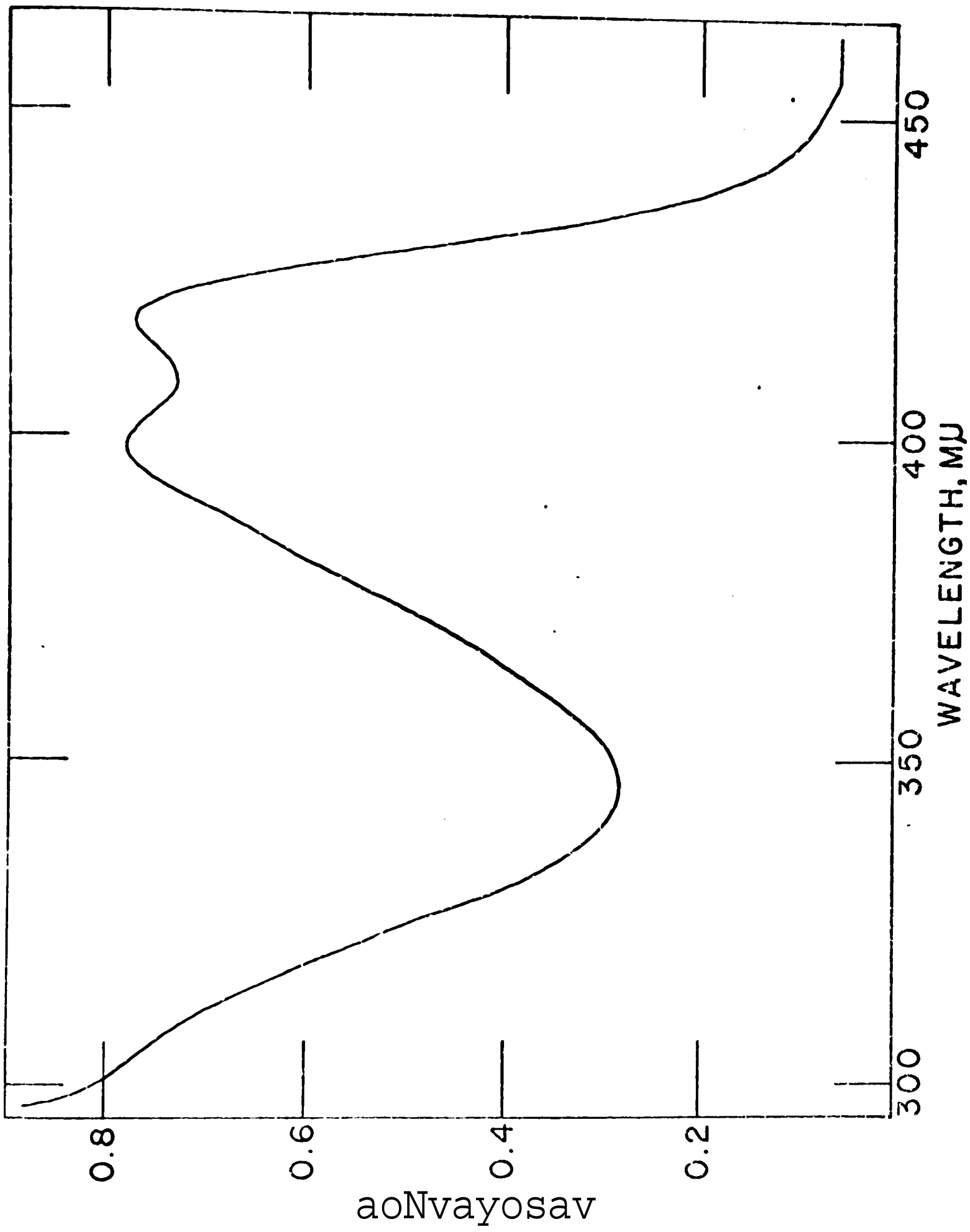
This hidden peak became a candidate for the charge-transfer complex band. It did not, however, behave as would be expected. As the reaction progressed, this band did not decrease in intensity although TCNE was being consumed in the reaction. This band also did not increase in any predictable way with increasing pyridine concentration.

It should be noted here that this band at 350 m μ could be an artifact since the method of analyzing the spectrum is not strictly valid.

Figure 5. Optical spectrum of the TCNE-pyridine system in
CH₂Cl₂ using a 10 mm. path-length cell.

[TCNE] = 5 X 10⁻⁴ M

[pyridine] = 0.2 M



To analyze the spectrum it was assumed that only the tricyanoethenolate ion was absorbing at 305 m μ and that only the PCNP ion was absorbing at 420 m μ . These assumptions are certainly open to question.

Several careful attempts were made to repeat the interaction in the vacuum system with complete exclusion of water and oxygen in order to prevent the formation of the PCNP and tricyanoethenolate ions. A spectrum from each of these systems, however, resembled that of Figure 5. If water or oxygen is required for the chemical reaction, apparently it cannot be removed in the small spectroscopic concentration required.

From the above observations, it is little wonder that other workers using undried reagents and solvents observed only the PCNP ion formation. With undried pyridine and without degassing, the reaction is very rapid and the PCNP doublet is the only absorbance seen in the spectrum.

Since it appeared that water could not be removed in the small concentrations necessary for this spectrophotometric method, the decision was made to use identical drying techniques while increasing the concentrations of pyridine and TCNE.

An optical cell was purchased from Pyrocell, Inc. with a light path length of 0.1 mm. which had a graded pyrex seal attached to the quartz cell. The pyrex connector allowed the cell to be connected to the vacuum apparatus. Using the thin cell, the concentrations were increased to:

$$[\text{TCNE}] = 0.03 \text{ M}$$

$$[\text{pyridine}] = 0.5 - 2.5 \text{ M}$$

It **was hoped** that this would make the absorbance due to the complex **much more intense** **In** comparison to the absorbances from the reaction **products**.

The optical spectra obtained with pyridine using the vacuum system **and the** thin cell are shown in Figure 6. A broad band appeared at 342 **my** **which** Increased in Intensity with increasing pyridine concentration. **This** band decreased with time and became distorted at about 420 **my** due **to the** formation of the PCNP ion. Since the peak at 342 **my** appeared **immediately** and disappeared as the reaction progressed, it is proposed **that** this absorbance is due to the charge-transfer complex.

The Increasing absorbances shown in Figure 6 were a result of increasing pyridine concentration. In the initial spectrum, very little distortion was evident from absorption by the reaction products. As the **additional** increments of pyridine were introduced, with corresponding **longer** time periods for the reaction to progress, the bands were more **distorted**. This formation of reaction products represented a decrease in TCNE concentration. The later peaks (more concentrated pyridine), therefore, were not as intense as would be expected from the initial **con-**
centration of TCNE. Any attempt to determine the equilibrium constants by a Benesi-Hildebrand-type method was more or less inaccurate depending upon the amount of reaction which had occurred when the spectrum was taken. Coupled with this is the fact that at most only three points **could** be obtained to determine the straight line necessary for calculation of equilibrium constants and extinction coefficients of the complex. In all of the methyl-substituted pyridine systems, only the first **two** spectra could be used for determining equilibrium constants because

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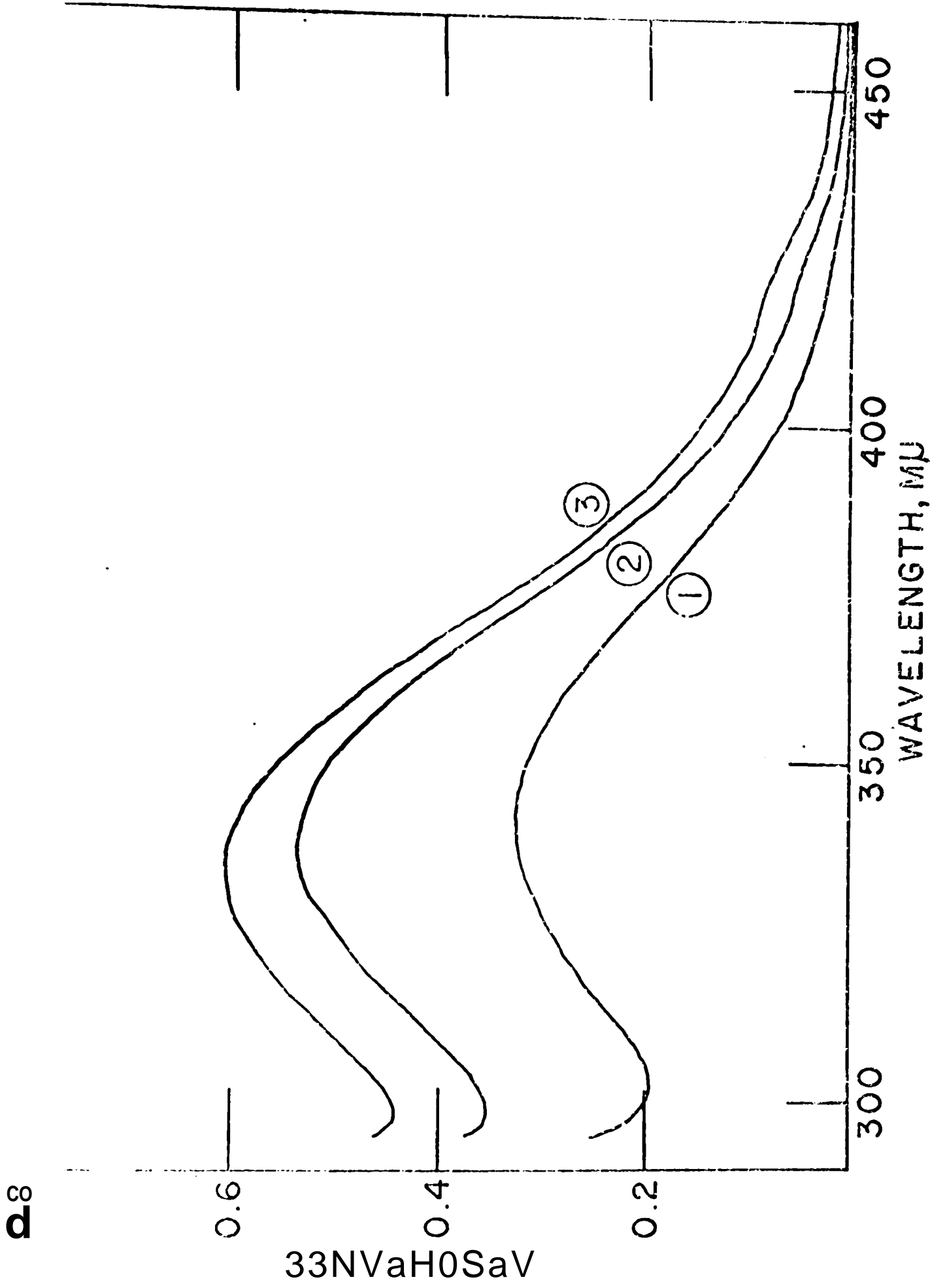
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s [au-ppjjXd]

W eO'O = [SNDI]

•Jiao qnSuax-q^Bd uim I'O ^ Sujsn ID HO

uf raaijsXs 3ujpTjXd-3NDI aq^ jo uinj^oads j^^T^do '9 ajnSxj



33NVaH0SaV

of extensive reaction product formation by the time the third increment of pyridine was added. Under these conditions, the equilibrium constants **and** extinction coefficients obtained for these complexes should be viewed as little more than mathematical exercise. Certainly no quantitative comparisons can be made which can be considered valid.

The wavelength of maximum absorbance for the complex band in the **pyridine** systems appeared to shift to shorter wavelengths with increasing pyridine concentration. This may either be a solvent shift as the fraction of pyridine becomes greater or it may be only an apparent shift due to increasing absorbance at 300 m μ . Formation of the tricyanoethenolate ion and the resulting absorbance at 300 m μ would not **only** intensify the complex peak slightly, but would also make it appear to shift to shorter wavelengths.

An attempt was made to decide between these two proposals by dissolving TCNE in neat pyridine under anhydrous vacuum conditions. The optical spectrum of this system showed a peak at 317 m μ . The peak **appeared** to decrease as the absorbance of the PCNP ion increased. It was felt that this might be the complex peak shifted to shorter wavelengths. In a separate experiment, TCNE was dissolved in neat pyridine, as earlier, to produce the 317-m μ peak. Then CHCl₃ was distilled into the system to form a 1:1 pyridine-CHCl₃ solvent. If the 317-m μ peak were the complex peak, dilution of the pyridine with CHCl₃ should have made the band shift to longer wavelengths. The peak, however, showed no such shift to longer wavelengths and even appeared to shift to shorter wavelengths. These data indicated that the 317-m μ peak might be a red-shifted tricyanoethenolate ion absorbance in pyridine. The spectrum

of the synthesized compound in pyridine, however, gave only a peak at about 300 m μ . The exact nature of the 317-m μ peak was not established.

Interactions of TCNE with 2-picoline, 4-picoline, 2,6-lutidine, 3,4-lutidine and 3,5-lutidine were carried out in an identical manner to that used for the pyridine system. The concentrations of reagents were kept the same for each system. In this way the spectra could be more easily compared without having to calculate equilibrium constants.

The optical spectra for the 4-picoline-TCNE system are shown in Figure 7. The broad peak appeared at 347 m μ with an initial absorbance somewhat more intense than that for the pyridine system. By the time the third spectrum had been recorded, a considerable amount of PCNP had been formed. This was evidenced not only by the absorbance at 420 m μ but also by the lack of any increase in the complex band even though the pyridine concentration had increased.

Figure 8 shows the optical spectra of the 2-picoline-TCNE system. The initial spectrum showed a broad weak absorbance with a poorly defined band at approximately 330-350 m μ . Addition of more 2-picoline increased the absorbance but did not further define the band.

The optical spectra for the complexes of TCNE with 3,5-lutidine and 3,4-lutidine are shown in Figures 9 and 10, respectively. The 3,5-lutidine-TCNE system shows a broad band at 355 m μ . By the time of the addition of the third increment of 3,5-lutidine, the reaction had progressed to the extent that the complex band intensity fell below that for the second spectrum. The third spectrum showed a distortion at about 400 and 420 m μ due to the PCNP ion formation. This spectrum also showed smaller distortions which appeared to correspond to the

Figure 7. Optical spectrum of the TCNE-4-picoline system in CH_2Cl_2 using a 0.1 mm. path-length cell.

[TCNE] = 0.03 M

[4-picoline] =

1. 0.5 M

2. 1.5 M

3. 2.5 M

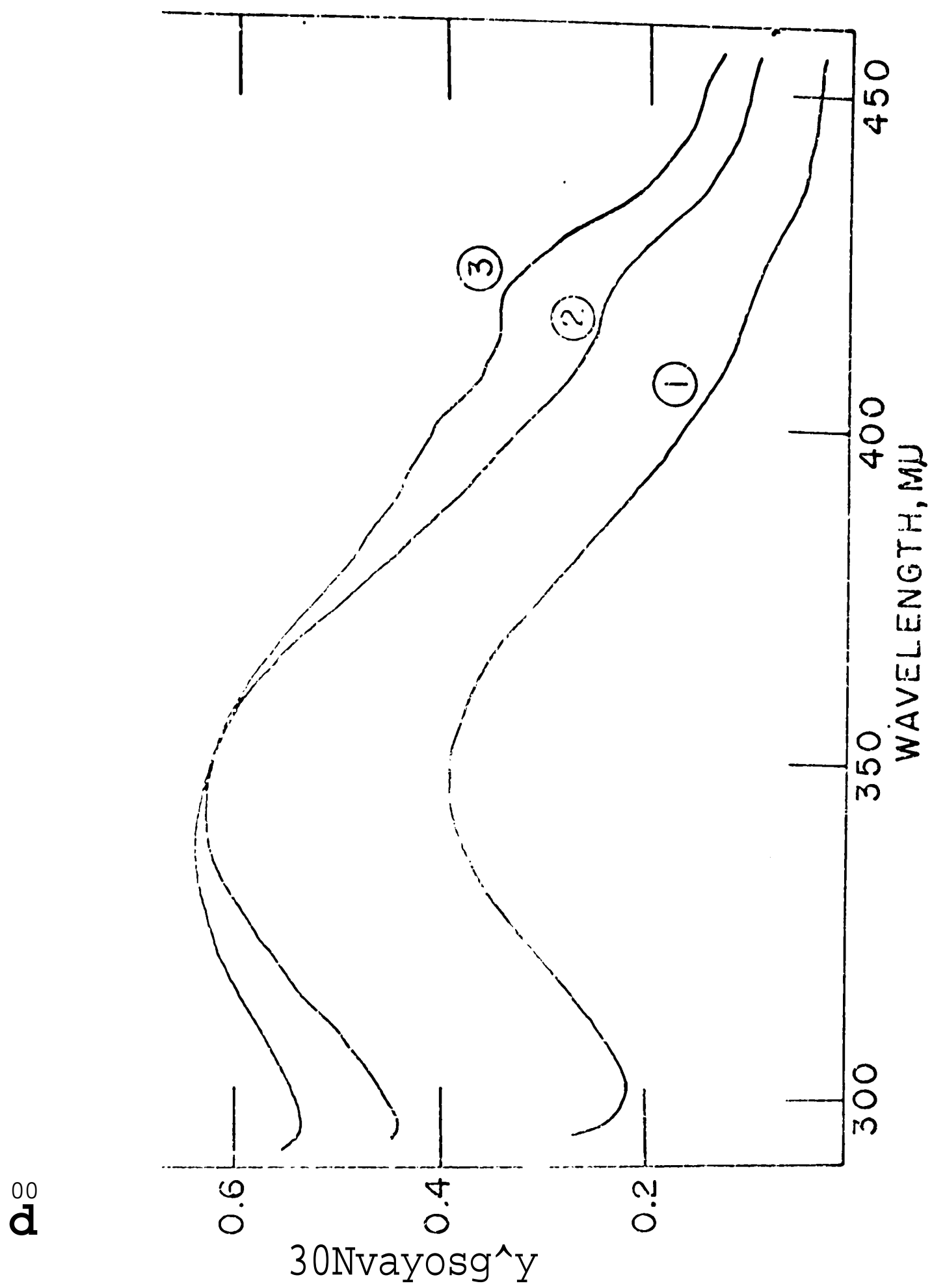


Figure 8. Optical spectrum of the TCNE-2-picoline system in CH_2Cl_2 using a 0.1 mm. path-length cell.

[TCNE] = 0.03 M

[2-picoline] =

1. 0.5 M

2. 1.5 M

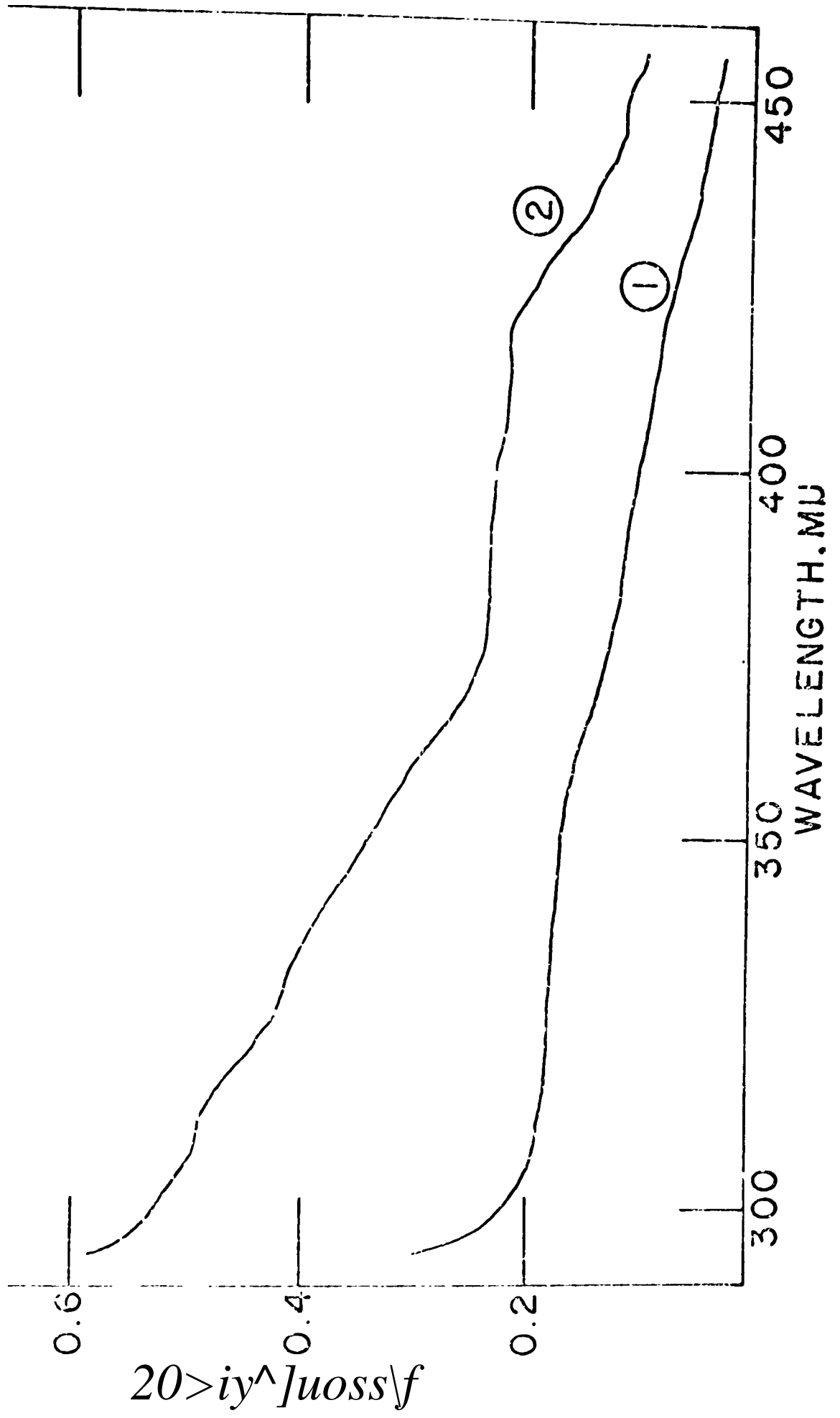


Figure 9- Optical spectrum of the TCNE-3,5-lutidine system in
CH₂Cl₂ using a 0.1 cm. path-length cell.

[TCNE] = 0.03 M

[3,5-lutidine] =

1. 0.5 M

2. 1.5 M

3. 2.5 M

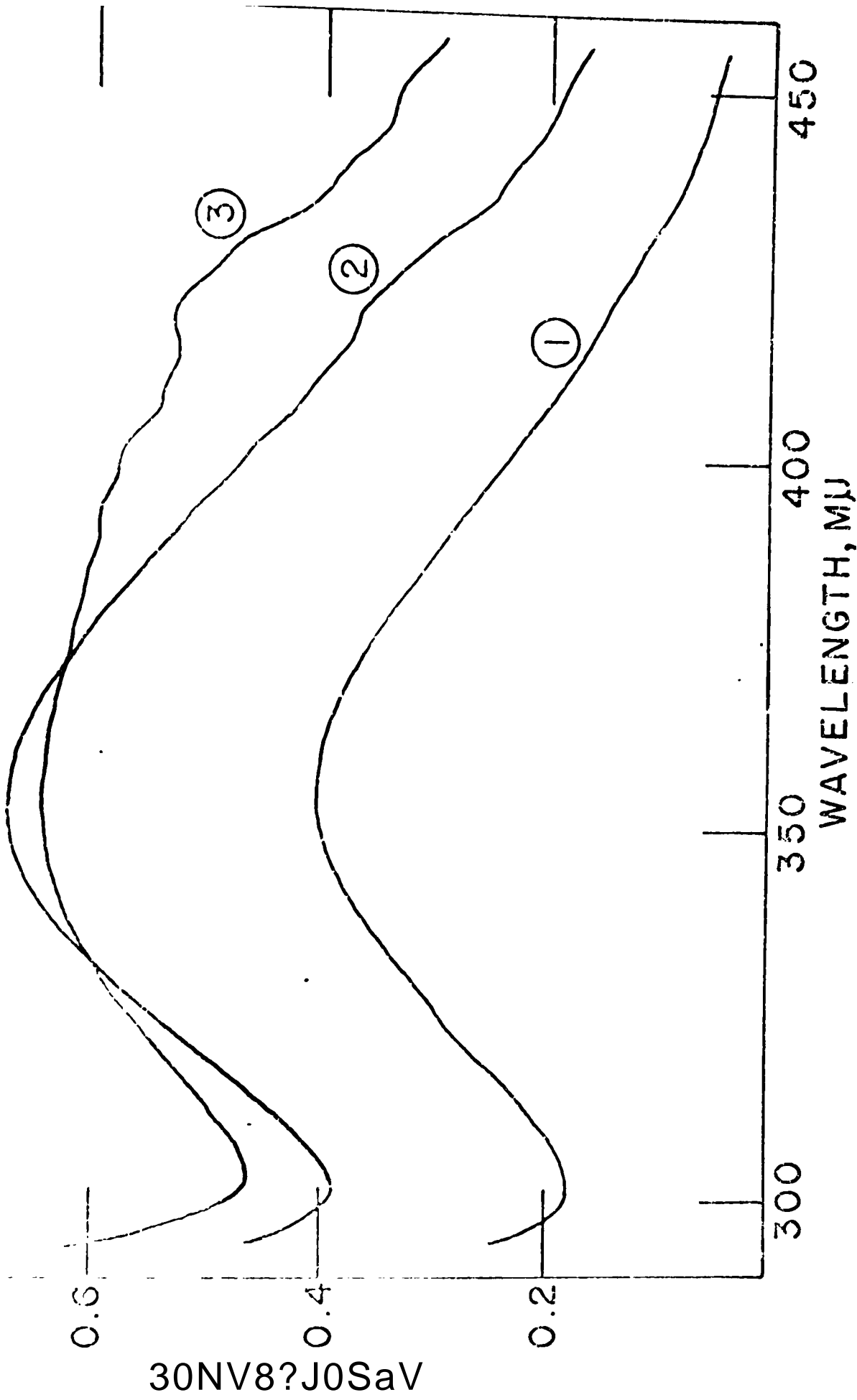


Figure 10. Optical spectrum of the TCNE-3,4-lutidine system In
CH Cl[^] using a 0.1 mm. path-length cell.

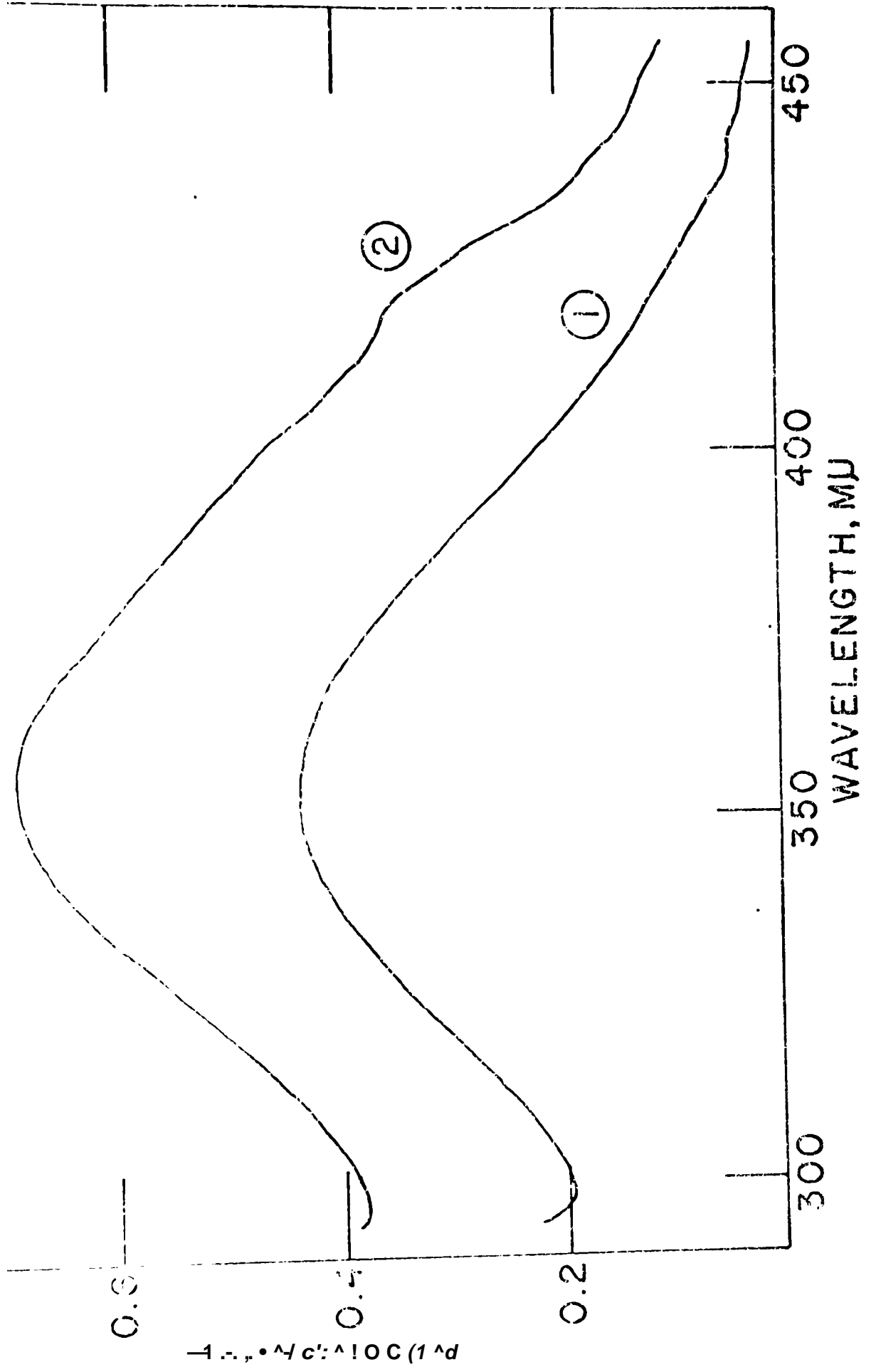
[TCNE] = 0-03 M

[3,4-lutidine] =

1. 0.5 M

2. 1.5 M

08



vibrational maxima of the TCNE anion radical. The spectra of the TCNE-3,4-lutidine system showed the band at 353 m μ with very little distortion after the two increments of base were added. The intensity of the initial bands of both complexes were greater than in the pyridine system with the 3,4-lutidine peak being slightly more intense than the 3,5-lutidine peak. The absorbance of the 3,5-lutidine peak was practically the same as that of the 4-picoline band.

The spectra of the TCNE-2,6-lutidine system are shown in Figure 11. Very weak absorbances were observed at 400-420 m μ and at about 300 m μ . No evidence was found, however, for a charge-transfer band in the region exhibiting absorbances in the other pyridine systems.

Although the equilibrium constants calculated for these complexes (Table I) are, at best, only approximate, it appears that one can draw some qualitative conclusions from the spectra of the TCNE-pyridine systems. There certainly appears to be some hindrance to complex formation by methyl-substitution in the positions adjacent to the nitrogen atom. This effect also appears to be more pronounced with disubstitution than with monosubstitution in these positions. It is proposed, therefore, that pyridine acts as an n-electron donor in its complexes with TCNE. The lack of complex formation with 2-picoline and 2,6-lutidine would then be due to a steric interference of approach of the molecule to the nitrogen atom of the base.

Assuming that the complex extinction coefficients for the pyridine and methyl-substituted pyridines are about equal, the absorbance of the initial spectrum of each complex can be used as a measure of the amount of complex formation. The initial spectrum is used since small amounts.

Figure 11. Optical spectrum of the TCNE-2,6-lutidine system in CH₂Cl₂ using a 0.1 mm. path-length cell.

[TCNE] = 0.03 M

[2,6-lutidine] =

1. 0-9 M

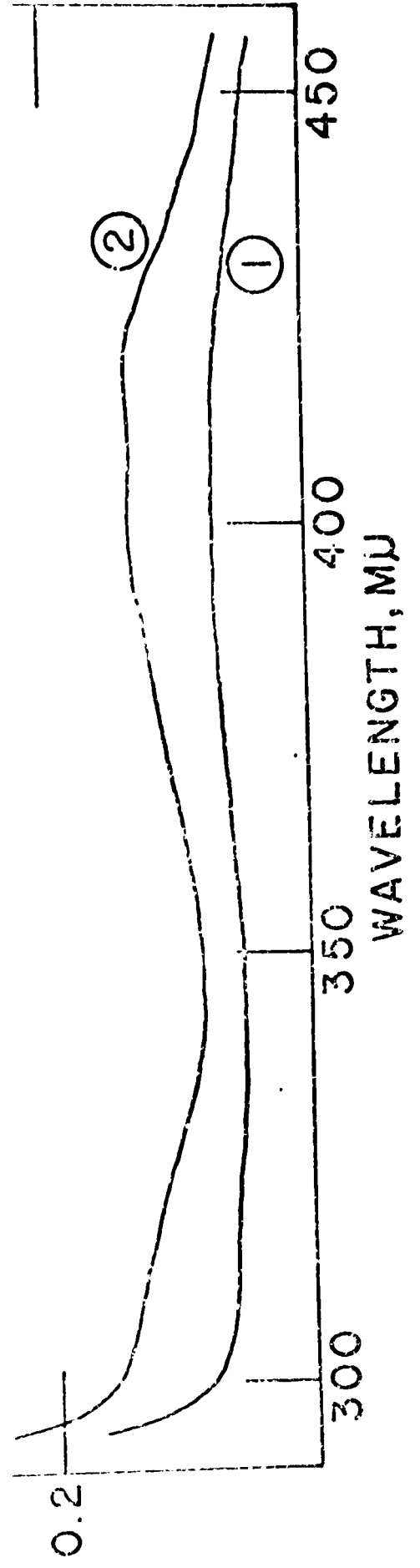
2. 1.9 M

α_{CD}

α_{CD}

M

30NVQ>J0SaV



of reaction products have distorted the spectrum or consumed TCNE at this point. These peaks decrease 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 very closely their basicities (Table III). Although this trend is not conclusive because of the uncertainty in the original assumption, these data are indicative of an n donor.

In view of Mulliken's proposal for the pyridine-I charge-transfer transition (34), it might appear that one cannot speak strictly of an n- or a π -electron donation. Mulliken noted, however, that TT contributions to the charge-transfer band did not alter the geometry of the complex expected for a n-electron donation. This theoretical proposal, therefore, does not appear to effect the conclusions reached for the pyridine-TCNE complex. Even if TT transitions contribute to the charge-transfer absorption, the complex geometry still appears to be that for an n-type complex.

Formation of the TCNE Anion Radical

In many of the interactions of TCNE with heteroatomic donors, the TCNE anion radical has been detected. In practically all of these cases, the ion formation was attributed to the dissociation of a charge-transfer complex with complete one-electron transfer. Very few of these systems, however, produced evidence of the formation of the cation radical necessarily formed by such a dissociation.

Liptay, Briegleb and Schindler (12) observed fairly conclusive spectrophotometric evidence of the simultaneous existence of the TCNE anion

radical and the tetramethylphenylenediamine cation radical.

Stewart, Eisner and Carper (25) ascribed the radical anion formation in their system to the dissociation of the DMSO-TCNE complex. However, Butler, Oakes and Symons (27) attributed the radical formation in their reinvestigation of the system to reduction by sulfide ion, a decomposition product of DMSO.

Nicolau and Cailly (38), in their esr study of the pyridine-TCNE system, obtained different esr spectra depending upon relative TCNE-pyridine concentrations and temperature. A singlet was recorded with high concentrations of TCNE. The nine-line spectrum of the TCNE anion radical was observed with low concentrations of TCNE and upon lowering the temperature. They noted that both esr signals had the same g-value. They concluded that the singlet was due to a paramagnetic complex species, presumably a triplet. The authors claimed that appearance of the TCNE anion radical at low temperatures showed that the dissociation of the complex was an exothermic process.

From esr studies in our system, we propose a simpler and more likely explanation. At relatively high concentrations of TCNE, the TCNE anion radical undergoes electron exchange with neutral TCNE molecules which broadens the esr hyperfine and only a singlet is observed. If the concentration of TCNE is decreased, the hyperfine appears. Also, lowering the temperature slows the rate of exchange and produces the hyperfine spectrum. This explanation requires only the presence of the TCNE anion radical.

The lack of evidence for the cation radical implies that the formation of the TCNE anion radical may not be from the dissociation of

a charge-transfer complex. Several workers have shown that TCNE is reduced to the anion radical by mild reducing agents such as T, SCN⁻ and several more. Webster, Mahler and Benson (46) showed that CN⁻ reduced TCNE in very good yields. The formation of both the tricyanoethenolate and pentacyanopropenide ions as observed in the TCNE-pyridine system liberates CN⁻ ions. Very possibly then, the TCNE anion radical arises from the CN⁻ reduction of TCNE. This is substantiated by some extent by our esr studies which show the concentration of anion radical to slowly increase over a period of hours. More careful investigation might show whether or not this increase paralleled the formation of reaction products.

Forness and co-workers (47) have shown that OH⁻ can also reduce TCNE. This ion may possibly bring about the production of the anion radical in our systems. A detailed study of the oxidation products in concentrated TCNE-pyridine systems might clarify this question.

TCNE-Thianthrene Charge-Transfer Complex

Thianthrene has a relatively low ionization potential and forms stable cation radicals in a variety of systems, and salts of the cation radical have been isolated (53). The TCNE charge-transfer complex has been observed by Foster and Hanson (21).. If this complex dissociated, the thianthrene cation radical formed might be stable enough to be detected by esr.

A study of this system in both CH₂Cl₂ and CH₃CN showed no esr signal. This could conceivably be due to a different type of complex formed in this case (IT complex). However, it is proposed here that the

TCNE anion radical Is not formed by the dissociation of the charge-transfer complex In our systems.

CHAPTER IV

SUMMARY AND CONCLUSIONS

1. **The** absorbance bands reported in the literature to be those **of the charge-transfer** complex **for** the TCNE-pyridine system are, in **fact, of the** pentacyanopropenide ion, a reaction product.
2. **Interaction** of TCNE with pyridine under anhydrous and degassed **conditions gave a** well-defined peak attributed to the charge-transfer **complex.**
3. **Bands were** also obtained with 4-picoline, 3,4-lutidine and **3,5-lutidine** as **donors.** No charge-transfer absorbance was found when **2,6-lutidine** was **the** donor. Only weak absorbance with a poorly defined maximum **was** obtained in the 2-picoline-TCNE system.
4. Qualitative comparisons of the spectra for the TCNE complexes **with** methyl-substituted pyridines show steric hindrance to complex formation by methyl substitution in the 2- or 6-position.
5. On **the** basis of a steric effect, it is proposed that in complex **formation the** pyridine acts as an n-electron donor.
6. **The** TCNE anion radical was obtained in the reaction of TCNE with **CN⁻ Ion.** Since **CN⁻** is liberated by chemical reactions in the TCNE-**pyridine** system, the formation of the TCNE anion radical is proposed **to be due to reduction** by **CN⁻** ion and not to the dissociation of the **charge-transfer** complex.

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APPENDIX

Benesl-Hildebrand Method for Determining Equilibrium Constants and Extinction Coefficients of Complexes (7)

One to one complex formation of the type of interest in this study can be represented by:



$$K = (DA)/(D)(A)$$

where (DA), (D) and (A) represent equilibrium concentrations of complex, donor and acceptor, respectively. Also,

$$K' = (DA)/[(D)^0 - (DA)][(A)^0 - (DA)]$$

where (D) and (A) represent initial concentrations of donor and acceptor. If the donor concentration is large in comparison to complex concentration, the following relationships are valid:

$$K = (DA)/[(D)^0][(A)^0 - (DA)]$$

$$(DA) = K(D)^0(A)^0/[1 + K(D)^0]$$

If only the complex absorbs at the wavelength chosen for analysis (usually λ_{max} for the complex), then

$$d = \epsilon L(DA)$$

where d is the absorbance, e is the extinction coefficient for the complex, and L is the cell path length.

The following equation may then be derived:

$$(A)^L/d - 1/Kc(D)^ + 1/e$$

If $(A)^L$ is held constant and (D) varied in a series of experiments, the K and e values may be determined graphically by plotting $(A)^L/d$ versus $1/(D)^$. This treatment yields a straight line whose intercept is $1/e$ and whose slope is $1/Kc$.

If the concentrations are expressed in moles/l., the units for K are l./mole and for e , l./mole cm. It is important to note that some workers express donor concentrations in terms of mole fraction rather than molarity (6,41). This yields a mole fraction equilibrium constant which is dimensionless and is numerically different than the molar equilibrium constant. The equilibrium constants obtained by Merrifield and Phillips (6) have been erroneously interpreted as molar equilibrium constants (8,9) resulting in invalid comparisons. Caution should be exercised, therefore, in comparing equilibrium constants by different workers.

Absorbance Data for Complexes with TCNE

[TCNE] - 0.03 M		0.1 mm path-length cell		
Donor	Wavelength (m μ)	Donor Concentration (M)	Absorbance	
pyridine	342	0.55	.328	
		1.55	.535	
		2.60	.600	
4-picoline	347	0.5	.396	
		1.5	.625	
		2.5	.628	
3,5-lutidine	355	0.5	.406	
		1.5	.674	
		2.5	.645	
3,4-lutidine	353	0.5	.438	
		1.5	.689	

Absorbance Data for the Thianthrene-TCNE Complex

10 mm. path-length cell

solvent: CH₂Cl₂

[TCNE] (M.)	[Thianthrene] (M.)	Absorbance (478 mμ)	Absorbance (610 mμ)
5 X 10 ⁻⁴	1 X 10 ⁻²	.028	.027
	2 X 10 ⁻²	.053	.049
	3 X 10 ⁻²	.075	.071
	5 X 10 ⁻²	.126	.119
	1 X 10 ⁻¹	.233	.218
1 X 10 ⁻³	5 X 10 ⁻²	.029	.028
		.055	.053
		.080	.076
		.131	.124
		.258	.242

