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SUBSTITUENT EFFECTS UPON THE
REACTIONS OF FERROCENE

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science.

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ABSTRACTARTHUR LAKES LIBRARY
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Several monosubstituted ferrocenes and one disubstituted ferrocene were prepared, and the oxidation potentials of these compounds were determined chronopotentiometrically. The deviation of acetamidoferrocene from Hammett correlation plots previously reported by Hall and Russell was verified.

Tetrachloroferrate (III) salts of ferrocene, acetylferrocene, acetamidoferrocene, and 1-1'-dichloroferrocene were prepared, and spectroscopic studies were performed on these compounds in the infrared and visible regions.

Infrared data obtained for the acetamidoferricenium cation indicate that there is no direct coordination between the non-bonded electron pairs on the oxygen atom with the positive iron atom. Such an interaction had been proposed by Hall and Russell in 1967 as an explanation for the anomalously low oxidation potential of acetamidoferrocene.

The visible absorption spectra of the ferricenium cation contains a moderately strong band at $617 \text{ m}\mu$. Prins assigned this band to a ligand to metal charge

transfer transition on the basis of shifts observed in the position of this band for the acetylferricenium and 1-1'-dimethylferricenium cations. In the present study substituent effects upon the visible absorption spectrum of the ferricenium cation were found to be in conflict with those reported by Prins for related compounds. These conflicting results leave Prins' band assignments for the ferricenium cation open to question.

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INTRODUCTION

Since the discovery of ferrocene (1, 2) in 1951 and the subsequent early detection (3) of the π -bonded or "sandwich structure" (Fig. 1) of the ferrocene molecule, a great amount of effort has been expended in attempting to elucidate the nature of the electronic interactions which occur in the ferrocene molecule. The disclosure (4) that the cyclopentadienyl rings of the ferrocene molecule possess aromatic character initiated an extensive study of electrophilic substitution reactions on ferrocene. These resulted in the synthesis of a large number of mono- and polysubstituted ferrocene derivatives. Literature pertinent to the development of ferrocene chemistry in its entirety is too exhaustive and diverse to warrant a thorough review in this thesis. Since good reviews (5, 6, 7) have been published by several authors, only those aspects of ferrocene chemistry directly applicable to the present research will be mentioned here.

One of the most characteristic reactions of ferrocene is its one electron oxidation (8) to form the ferricenium cation. In 1959 Kuwana and coworkers (9) reported

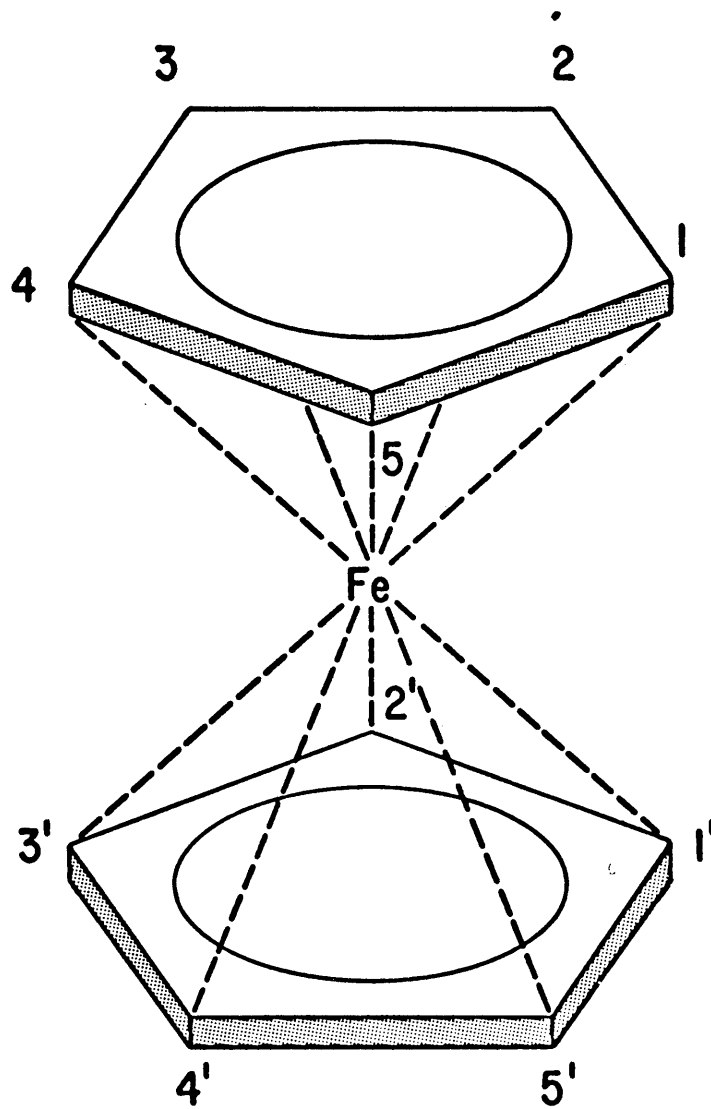


Figure 1. The Structure of ferrocene.

oxidation potentials for a number of ferrocene derivatives determined chronopotentiometrically in acetonitrile. These workers observed a correlation between the relative ease of oxidation and the electron donating or withdrawing character of the substituent attached to the ferrocene molecule. Further, they stated that substituent effects on oxidation potentials of ferrocene compounds appeared to be additive. In 1960 the same research group (10) proposed that the oxidation-reduction chemistry of the metallocenes should closely parallel reactions of ferrocene derivatives toward electrophilic substitution. More easily oxidized compounds should be those which possess a greater electron density around the ferrocene nucleus, and thus are more reactive toward electrophilic substitution.

Hall and Russell (11) reported in 1967 chronopotentiometric quarter wave potentials for 15 ferrocene derivatives measured in acetonitrile. These workers demonstrated by means of statistical analyses that the quarter wave potentials were correlated with the Hammett σ_p constants (12), but that they were best correlated with the blended constant $(\sigma_m + 2\sigma_p)/3$. These results were interpreted as an indication that the Hammett σ_p constants overestimate the importance of resonance effects in the chronopotentiometric oxidation of ferrocene derivatives. This conclusion is in agreement with Russian workers (7),

but it is in disagreement with Little and coworkers (13, 14). However, a more important observation which resulted from this work was that acetamido- and urethanoferrocenes deviated markedly and uniformly from the regression lines in all plots. In each case the deviation was in the direction of a more negative oxidation potential, indicating that the acetamido and urethano substituents are more powerful electron donating groups in the ferrocene system than in the benzene system (15, 16).

In 1963 Hall and Richards (17) reported that the acylation of acetamido- and urethanoferrocenes yielded predominately heteroannularly (eg., 1-1'-positions shown in Fig. 1) substituted isomers. Formation of predominately heteroannularly substituted products suggested that these substituents were deactivating the cyclopentadienyl rings toward electrophilic substitution. Further confirmation of the deactivating effect of the acetamido group was derived from the competitive acylation of ferrocene and acetamidoferrocene. In this reaction ferrocene was found to be more reactive than acetamidoferrocene by approximately a factor of two. These results were completely unexpected in view of the facile oxidation reaction. Hall and Richards (17) proposed that the conflicting results obtained for the oxidation reaction and the electrophilic substitution reaction were due to complex formation between the Lewis acid catalyst employed in the latter

reaction and the acetamido group.

Hall and Russell (11) postulated that acetamido- and urethanoferrocenes were more easily oxidized than predicted because of an "internal solvation" effect. This phenomenon involved coordination of the non-bonding electron pairs on the carbonyl oxygen atom with the positive iron atom (Fig. 2). The increased stability of the acetamido- and urethanoferrocenium cations permitted the oxidation of the corresponding neutral ferrocene compounds at anomalously low potentials.

Komenda and Tirouflet (18) observed no unusual behavior for acetamidoferrocene when it was oxidized polarographically in a 50 percent ethanol-water solution containing 1 M perchloric acid. The data point for this compound fell very nearly on the correlation line when oxidation potentials for 17 ferrocene derivatives were plotted versus the Hammett σ_p constants.

The concept of direct interaction between ring substituent and the iron atom of the ferrocene molecule has perviously been discussed by several other research groups. A few examples are presented below.

Hoh and coworkers (19) reported chronopotentiometric quarter wave potentials for a limited number of mono- and disubstituted ferrocenes determined in acetonitrile. These workers were unable to correlate the quarter wave potentials of acetylferrocene, trimethylsilylferrocene,

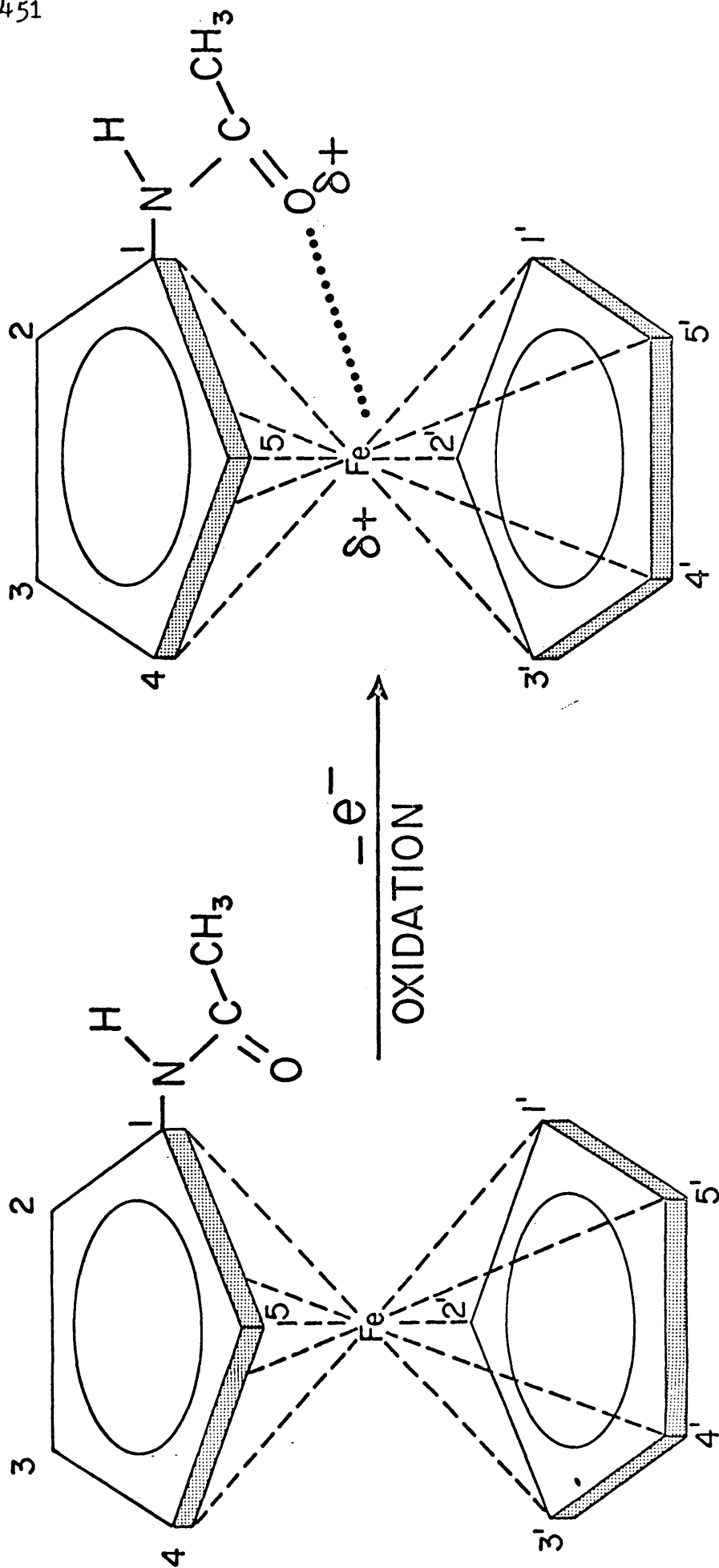


Figure 2. "Internal Solvation" as proposed by Hall and Russell (11).

and 1-1'-di(trimethylsilyl)ferrocene with either the Hammett σ_m (20) or the Taft σ^* (21) constants. In both cases the points deviated from the regression lines in the positive direction, indicating an enhanced stability toward oxidation. A tentative explanation given for this behavior was interaction of the π -orbitals of the acetyl group and the empty d-orbitals of the silicon atom with the π -orbitals of the cyclopentadienyl rings or the molecular orbitals centered around the iron atom.

Existence of a direct field effect between ring substituents and the iron atom in ferrocene was also proposed by Gubin and Perevalova (22) in 1962. These workers determined the formal oxidation potentials for a number of monosubstituted ferrocenes by titration with potassium dichromate in an acetic acid-perchloric acid solvent. Correlation of the formal oxidation potentials with the σ_n (23) constants required two straight lines, separating the ferrocene compounds into two distinct groups. Ferrocenes with halo, carboxy, and carboethoxy substituents were suspected of possessing a direct field stabilization. This interpretation was, however, later questioned by Little and coworkers (13).

Nesmeyanov and Perevalova (7) observed a diminishment of electron withdrawing properties when the halogens were attached to the ferrocene molecule. These workers proposed the formation of a dative bond between the

d-electrons of the halogens and the empty d-orbital of the iron atom to account for this observation.

It was the purpose of the research described in this thesis to prove whether the "internal solvation" mechanism proposed by Hall and Russell (11) was, indeed, the reason why acetamidoferrocenes oxidize at unexpectedly low potentials. Little and coworkers (13) have used substituted ferrocenes to derive secondary σ constants. The validity of these constants is questionable if the "internal solvation" mechanism is operative with certain substituents.

EXPERIMENTAL WORK

Chemical Analysis

Carbon, hydrogen, nitrogen, chlorine, and iron analyses were performed by Huffman Laboratories, Inc., Wheatridge, Colorado.

Melting Points

Melting points were determined on a Thomas Hoover Melting Point Apparatus (Arthur H. Thomas Company, Philadelphia, Pa.). Particularly air sensitive compounds were placed in sealed capillary tubes. All melting points are uncorrected.

Instrumentation

Microbalance

A Cahn Model M10 Electrobalance was used to weigh out mg quantities of materials.

Chronopotentiometry

All of the chronopotentiometric measurements were performed at Western Washington State College under the direction of Dr. Donald M. King. Solutions of approx-

imately 2 mM concentration in the ferrocene compound and 0.20 M in anhydrous sodium perchlorate were prepared in acetonitrile. These solutions were run at a cell current of 0.054 ma and with a working platinum electrode surface area of 0.20 sq cm. The chronopotentiometric quarter wave potentials determined in this study were reproducible within 5 mv. Good reviews of the theoretical and practical considerations of chronopotentiometry are readily available (24, 25, 26, 27).

Infrared Spectroscopy

Infrared spectra were recorded on a Perkin-Elmer 521 Grating Infrared Spectrophotometer. Solution analyses were made using either matched sodium chloride or Irtran-4 cells of 0.2 cm pathlength. Both acetonitrile and dichloromethane were used as solvents. Solid state spectra of compounds were determined on KBr pellets. Approximately 1.0-2.0 mg of the compound and 250-300 mg of KBr were thoroughly ground in a mortar, and were then pressed into a pellet at a pressure of 20,000 psi. The KBr pellets measured about 10 mm in diameter and 1 mm in thickness. Solid state spectra were recorded from 4,000-300 cm^{-1} , since potassium bromide does not absorb infrared radiation in this region. All spectra were calibrated with a 0.05 mm Perkin-Elmer Polystyrene Film.

Ultraviolet and Visible Spectroscopy

Ultraviolet and visible spectra were recorded on a Beckman DK 2-A Ratio Recording Spectrophotometer. Solution analyses were made using matched 1 cm Beckman Standard Silica Cells (220-2500 $m\mu$ range) fitted with ground glass stoppers.

Reagents and Solvents

Ferric Chloride

Anhydrous ferric chloride, sublimed, from Matheson, Coleman, and Bell, was used as received.

Nitrogen

Nitrogen, prepurified, from the Linde Division of Union Carbide, was used as received.

Sodium Perchlorate

Anhydrous sodium perchlorate, reagent grade, from G. Frederick Smith Chemical Company, was used as received.

Acetamidoferrocene

The acetamidoferrocene (17) used in this study was donated by David W. Hall. This compound was used without further purification (mp 169.5-170°; lit. (17, 28) mp 173-173.5° and 170.5-172°).

Acetonitrile

Acetonitrile, analytical reagent, from Mallinckrodt Chemical Works, was purified according to the procedure

described by Forcier and Olver (29) prior to use as a chronopotentiometric and spectroscopic solvent.

Acetylferrocene

Acetylferrocene, from Research Organic/Inorganic Chemical Corporation, was recrystallized from hexane several times prior to use (mp 83-84°; lit. (30) mp 85-86°).

Butylferrocene

Butylferrocene, from Research Organic/Inorganic Chemical Corporation, was filtered through glass wool prior to use.

Dichloromethane

Dichloromethane, analytical reagent, from Mallinckrodt Chemical Works, was distilled over molecular sieves (Type 4A, Fisher Scientific Company) prior to use as a spectroscopic solvent.

Ferrocene

Dicyclopentadienyliron, practical grade, from Eastman Kodak Company, was recrystallized from benzene several times prior to use (mp 168-169°; lit. (30) mp 172.5-173°).

Water

Deionized water (Illinois Water Treatment Company, serial number MB-11926, Rockford, Ill.) was distilled

under nitrogen prior to use as a spectroscopic solvent.

Acetoxyferrocene

Acetoxyferrocene (31) was prepared by the addition of cupric acetate to a water solution of ferrocenylmonoboronic acid (31). The reaction mixture was extracted 3 times with 50 ml portions of ether, and the ether extracts were combined and evaporated to dryness under vacuum. The residue was extracted twice with 25 ml portions of hexane, and the hexane extracts were combined and evaporated to dryness under vacuum. The resulting residue was recrystallized from hot ethanol to give yellow-orange crystals (mp 58-60°; lit. (31) 64.5-66°).

Additional confirmation of the identity of this compound was made by comparing its infrared spectrum with that previously obtained using a pure sample of acetoxyferrocene (32).

Bromoferrocene

Bromoferrocene (33) was prepared by the addition of N-bromosuccinimide to a solution of chloromercuriferrocene (Research Organic/Inorganic Chemical Corporation) in DMF. The reaction mixture yielded bright, yellow crystals of Bromoferrocene (mp 31.5-32.5°; lit. (33) 32-33°).

1-1'-Dichloroferrocene

1-1'-Dichloroferrocene was prepared in a manner

very similar to the synthesis of polychlorinated ferrocenes described by Hedberg and Rosenberg (34). To a solution of ferrocenyllithium (35) in hexane at dry ice-acetone temperature was added 90 g of hexachloroethane (Eastman Kodak Company, practical grade) in 300 ml of a 50 percent THF-ether solution. After the addition was complete, the reaction mixture was allowed to come to room temperature. The reaction mixture was then poured into 100 ml of a 10 percent sodium bicarbonate solution and stirred vigorously. A black, tarry precipitate separated from the solution and was removed by vacuum filtration. The resulting filtrate was extracted with ether, and the ether extracts were combined and evaporated to dryness under vacuum. The residue was taken up in 200 ml of ether, and the resulting solution was filtered. Refrigeration of the filtrate overnight at approximately 5°C yielded 16 g of dark colored hexachloroethane, which was separated by vacuum filtration. The filtrate was reduced in volume under vacuum and chromatographed on a 15x35 cm alumina column. One large band moved down the column when hexane was used as eluent. The last 1/5 of the bright yellow band was collected and reduced in volume under vacuum. This solution was refrigerated at 5°C and produced dark-yellow crystals of 1-1'-dichloroferrocene (mp 77-79°; lit. (31) mp 75-77°). The remaining 4/5 of the bright yellow band contained

primarily ferrocene.

Ethylferrocene

Ethylferrocene was prepared by the reduction of acetylferrocene with lithium aluminum hydride (36). To a solution of 6.6 g of aluminum chloride in 100 ml of ether was added 1.9 g of lithium aluminum hydride suspended in 125 ml of ether. After the addition was complete, 9.0 g of acetylferrocene in 150 ml of THF was added to this solution over a period of 45 min. The solution was stirred for an additional 20 min after the addition of the acetylferrocene was complete. Excess lithium aluminum hydride was destroyed by the cautious addition of 200 ml of water to the reaction flask, followed by 50 ml of 6 N sulfuric acid. Two phases formed upon the addition of the water. The aqueous phase was extracted several times with ether, and the ether extracts were combined with the organic phase. The organic phase was then dried over anhydrous magnesium sulfate, reduced in volume under vacuum to 15 ml, and chromatographed on alumina. One large, red band moved down the column when hexane was used as eluent. This red band was collected and the hexane removed under vacuum. The residue which remained was a dark-red oil. This red oil was distilled in a micro-distillation apparatus at 4 mm pressure, and the fraction distilling at 97-101° was collected.

Preparations

Ferricenium Tetrachloroferrate (III)

Ferricenium tetrachloroferrate (III) was prepared by the addition of ferrocene to a solution of anhydrous ferric chloride in anhydrous ether (37). The bluish-green salt which precipitated was separated by vacuum filtration and recrystallized from hot ethanol. The ethanol solution yielded dark-blue crystals which did not melt or decompose up to 225°. Calculated for $C_{10}H_{10}Fe_2Cl_4$: C, 31.31%; H, 2.63%; Fe, 29.11%; Cl, 36.96%. Found: C, 31.20%; H, 2.68%; Fe, 29.17%; Cl, 36.60%.

The recrystallization was allowed to proceed for only 1 hr. A previous attempt to prepare ferricenium tetrachloroferrate (III) was unsuccessful when a recrystallization time of 3 weeks was used. In this case a compound which corresponded roughly to ferricenium trichloroferrate (II) was formed which had a mp of 174-175°. Calculated for $C_{10}H_{10}Fe_2Cl_3$: C, 34.48%; H, 2.88%; Fe, 32.09%; Cl, 30.55%. Found: C, 33.63%; H, 2.80%; Fe, 28.89%; Cl, 30.62%. Aharoni and Litt (38) reported that ferricenium trichloroferrate (II) could be prepared by the oxidation of ferrocene in methyl ethyl ketone with anhydrous ferric chloride in the presence of excess ferrocene. These workers also reported that the trichloroferrate (II) salt did not melt or decompose at temperatures up to 300°. It is possible that ferricenium tetrachloro-

ferrate (III) undergoes slow decomposition when it is exposed to protic solvents for lengthy periods of time.

Acetylferricenium Tetrachloroferrate (III)

Acetylferricenium tetrachloroferrate (III) was prepared by the addition of acetylferrocene to a concentrated solution of anhydrous ferric chloride in anhydrous ether. To 250 ml of anhydrous ether was added 10.0 g of anhydrous ferric chloride. This solution was filtered to remove the red particles which remained suspended in solution, and 0.4 g of acetylferrocene in 100 ml of anhydrous ether was added to the filtrate. At the start of the addition there was immediate formation of a bluish-green precipitate, which appeared to dissolve when the solution was stirred. When the addition was complete, the solution had changed from an initial dark reddish-brown to a dark-green color. This solution was cooled to about 5°C for a period of 3 hr. After this time the bottom of the flask was coated with finely-divided, dark-green particles upon which large, green needle crystals had formed. The reaction flask was swirled to free the needle crystals, and these were separated from the solution by vacuum filtration. No special precautions were taken to exclude air or moisture from the reaction flask, and optimization of the yield was not attempted. Calculated for $C_{12}H_{13}Fe_2Cl_4O$: C, 34.04%; H, 2.83%; Fe, 26.16%;

Cl, 33.22%. Found: C, 33.98%; H, 2.99%; Fe, 26.47%;

Cl, 33.49%. This compound had a mp of 92.5-93.5°.

Acetamidoferricenium Tetrachloroferrate (III)

Acetamidoferricenium tetrachloroferrate (III) was prepared in a manner analogous to the preparation of acetylferricenium tetrachloroferrate (III), but with slight modifications. Approximately 1.5 g of anhydrous ferric chloride was dissolved in 700 ml of anhydrous ether. This solution was placed in a 1000 ml round-bottomed flask attached to a Soxhlet extraction funnel containing 0.05-0.1 g of acetamidoferrocene. Extraction was carried out for 1 hr. The resulting dark-brown solution was filtered to remove suspended particles, and the filtrate was reduced in volume under vacuum to 250 ml. The solution was then cooled at 5°C for a period of 3 hours, during which time 40 mg of dark-red needle crystals separated from the solution. Calculated for $C_{12}H_{13}Fe_2Cl_4NO$: C, 32.70%; H, 2.97%; Fe, 25.34%; Cl, 32.18%; N, 3.18%. Found: C, 32.79%; H, 3.09%; Fe, 25.66%; Cl, 32.54%; N, 3.11%. The mp of this compound was 118-119°. No attempt was made to recover any acetamidoferricenium tetrachloroferrate (III) which remained in solution. The crystals did not appear to be either air or moisture sensitive, since no special precautions were taken during preparation and isolation.

1-1'-Dichloroferricenium Tetrachloroferrate (III)

1-1'-Dichloroferricenium tetrachloroferrate (III) was prepared by the addition of 0.1 g of 1-1'-dichloroferrocene in 75 ml of anhydrous ether to a filtered solution of 5.0 g of anhydrous ferric chloride in 100 ml in anhydrous ether. The addition was carried out with stirring, and the color of the solution changed from an original dark-brown to a dark-green color with no formation of a precipitate. This solution was kept at 5°C overnight, and during this time dark-green needle crystals had formed on the bottom of the flask. Suspended in the supernatant were finely-divided, dark-brown particles. To obtain the crystals in pure form, the ether solution containing the dark-brown particles was decanted from the flask, and the crystals remaining in the bottom of the flask were washed twice with 20 ml portions of cold ether. These crystals were then loosened from the bottom of the flask and recovered by vacuum filtration. The dark-green needle crystals obtained did not melt or decompose at temperatures up to 225°. Calculated for $C_{10}H_8Fe_2Cl_6$: C, 26.46%; H, 2.00%; Fe, 24.62%; Cl, 46.90%. Found: C, 26.61%; H, 2.00%; Fe, 24.98%; Cl, 46.16%. No special precautions were taken to exclude air or moisture from the reaction flask.

Attempted Preparation of Ethylferricenium Tetrachloroferrate (III)

The preparation of ethylferricenium tetrachloroferrate (III) was attempted by the addition of 2.0 g of ethylferrocene in 100 ml of anhydrous ether to a filtered solution of 10.0 g of anhydrous ferric chloride in 250 ml of anhydrous ether. At the start of the addition there was immediate formation of a dark-green precipitate on the walls and the bottom of the reaction flask. The solution was stirred for 5 min after the addition was complete. The ether solution was decanted from the flask, leaving the dark-green precipitate behind. Approximately 75 ml of ethanol was added to the reaction flask, and the flask was heated to dissolve the precipitate. Cooling the solution at 5°C overnight produced dark-blue crystals which were separated by vacuum filtration. Calculated for $C_{12}H_{14}Fe_2Cl_4$: C, 35.00%; H, 3.43%; Fe, 27.13%; Cl, 24.44%. Found: C, 37.34%; H, 3.71%; Fe, 30.89%; Cl, 27.81%. This compound had a mp of 112-113°. Since elemental analysis demonstrated that the tetrachloroferrate (III) compound had not been formed, the calculations for ethylferricenium trichloroferrate (II) were performed. Calculated for $C_{12}H_{14}Fe_2Cl_3$: C, 38.30%; H, 3.75%; Fe, 29.68%; Cl, 27.81%. Although there is a better correlation with the trichloroferrate (II) compound, positive identification of the anion involved was not made. However, infrared spectroscopy confirmed the presence of the ethylferricenium cation.

RESULTS AND DISCUSSION

Chronopotentiometric Studies

Chronopotentiometric quarter wave potentials for ferrocene, butylferrocene, acetoxyferrocene, acetamidoferrocene, bromoferrocene, and 1-1'-dichloroferrocene were determined in acetonitrile as described above. Table 1 lists the data which were obtained.

It has become customary to utilize the quarter wave potentials of substituted ferrocenes as the difference in their potentials relative to that of ferrocene. The magnitude and sign of the $\Delta E_{\frac{1}{4}}$ values give a direct indication of substituent effects upon oxidation potentials of ferrocene derivatives. Converting quarter wave potentials to $\Delta E_{\frac{1}{4}}$ values also allows the direct comparison of data among research groups.

The quarter wave potentials for bromoferrocene and 1-1'-dichloroferrocene have not been previously reported. In 1968 Hall and coworkers (39) reported the correlation of the solvolysis rates of heteroannularly substituted methylferrocenylcarbinyl acetates with the quarter wave potentials for the ferrocene derivatives corresponding to

Table 1. Chronopotentiometric quarter wave potentials for several ferrocene derivatives.

<u>Compound</u>	$E_{1/4}$	$\Delta E_{1/4}$
Acetamidoferrocene	0.260	-0.076
Butylferrocene	0.279	-0.057
Ferrocene	0.336	0.000
Acetoxyferrocene	0.385	+0.049
Bromoferrocene	0.509	+0.173
Acetylferrocene	0.589	+0.253
1-1'-Dichloroferrocene	0.649	+0.313

the acetates. A $\Delta E_{\frac{1}{4}}$ for bromoferrocene of 0.155 v was calculated using the quarter wave potentials of acetylferrocene, 1'-acetylbromoferrocene, and 1-1'-dibromoferrocene, assuming that substituent effects are additive in the oxidation reaction (9, 13). These authors reported a correlation coefficient of 0.995 for their data. Visual inspection of their plot (Fig. 3) indicates that an even better correlation of the data would be obtained if the $\Delta E_{\frac{1}{4}}$ for bromoferrocene of 0.173 v found in the present study were used.

Little and coworkers (13) reported in 1964 that acetoxy- and phenoxyferrocene were irreversibly oxidized. These workers observed that chronopotentiometric waves for these compounds were discontinuous, and that the $E_{0.22}$ values obtained upon current reversal differed from the estimated values for the quarter wave potentials of the forward waves. The magnitude and direction of this deviation was not reported.

The chronopotentiometric waves obtained for acetoxyferrocene in the present study were smooth and contained no discontinuities. Checks were made on the reversibility of the oxidation reaction for acetoxyferrocene, and it was found that acetoxyferrocene showed only slightly more irreversible character than did butylferrocene. Alkylferrocenes have been previously shown (10) to be reversibly oxidized chronopotentiometrically.

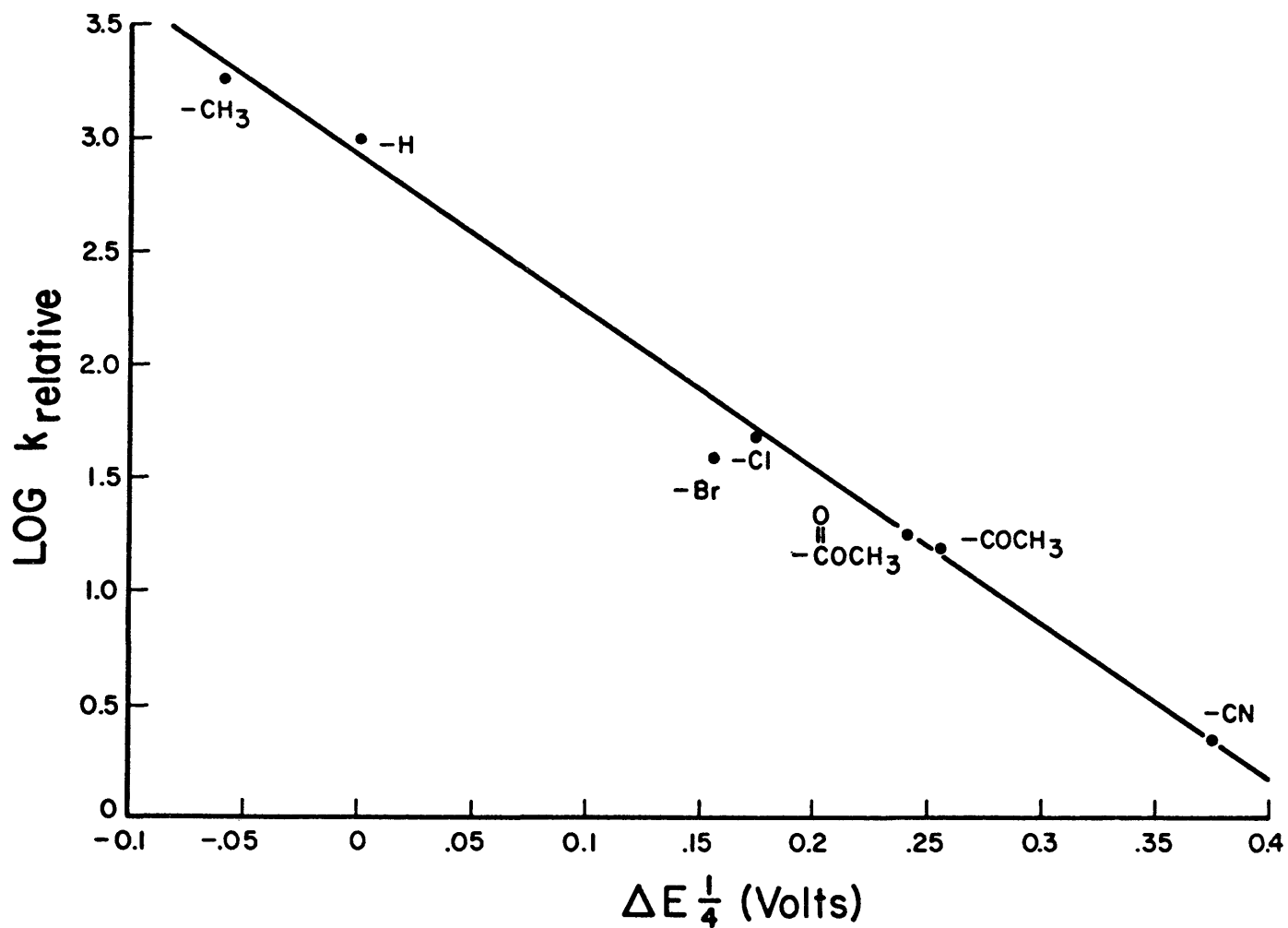


Figure 3. The correlation plot of Hall and coworkers for the solvolysis rates of heteroannularly substituted methylferrocenylcarbonyl acetates with the quarter wave potentials (39).

Gubin and Perevalova (22) determined the formal oxidation potentials of a number of monosubstituted ferrocenes by potentiometric titration with potassium dichromate in an acetic acid-perchloric acid solvent. They reported a value of +0.091 v for the oxidation potential of acetoxyferrocene with respect to ferrocene, and no mention was made of any difficulty with this determination.

It should be emphasized, however, that the acetoxyferrocene used in the present study had a low mp and was not submitted for analysis. It would appear that a definite confirmation of the reversibility of the oxidation of acetoxyferrocene must await detailed studies using material of proven purity.

Hall and Russell (11) reported in 1967 chronopotentiometric quarter wave potentials for 15 mono- or disubstituted derivatives determined in acetonitrile. The $\Delta E_{\frac{1}{4}}$ value of -0.068 v for acetamidoferrocene indicated that the acetamido group was much more electron donating in the ferrocene system than predicted by the Hammett constants derived from the reactions of benzene derivatives. This observation conflicts with the work of Komenda and Tirouflet (18), who reported that acetamidoferrocene fell on the correlation line when the oxidation potentials for a number of monosubstituted ferrocenes, determined polarographically in an aqueous ethanol-

perchloric acid solvent, were plotted versus the Hammett σ_p constants.

The $\Delta E_{\frac{1}{4}}$ values determined for acetamidoferrocene, acetylferrocene, and butylferrocene in the present study agree quite well with the values reported by Hall and Russell (11). Although these workers did not report a value for butylferrocene, they did give a value of -0.061 v for ethylferrocene. It has been demonstrated (40) that the ethyl and butyl groups have nearly identical electron donating properties in reactions of benzene derivatives. The results of the present study, then, confirm the deviation of acetamidoferrocene from Hammett correlation plots.

Figures 4 and 5 demonstrate the deviation of acetamidoferrocene from the regression line when the quarter wave potentials for 12 monosubstituted ferrocene compounds (Tab. 2) are plotted versus the σ_p° constants (41, 42, 43). The regression line in Fig. 4 was drawn omitting the quarter wave potential for acetamidoferrocene, while the regression line in Fig. 5 was drawn including the quarter wave potential for acetamidoferrocene. The statistical evaluation contained in Tab. 3 shows that a better correlation is obtained when the quarter wave potential for acetamidoferrocene is excluded.

Infrared Spectroscopic Studies

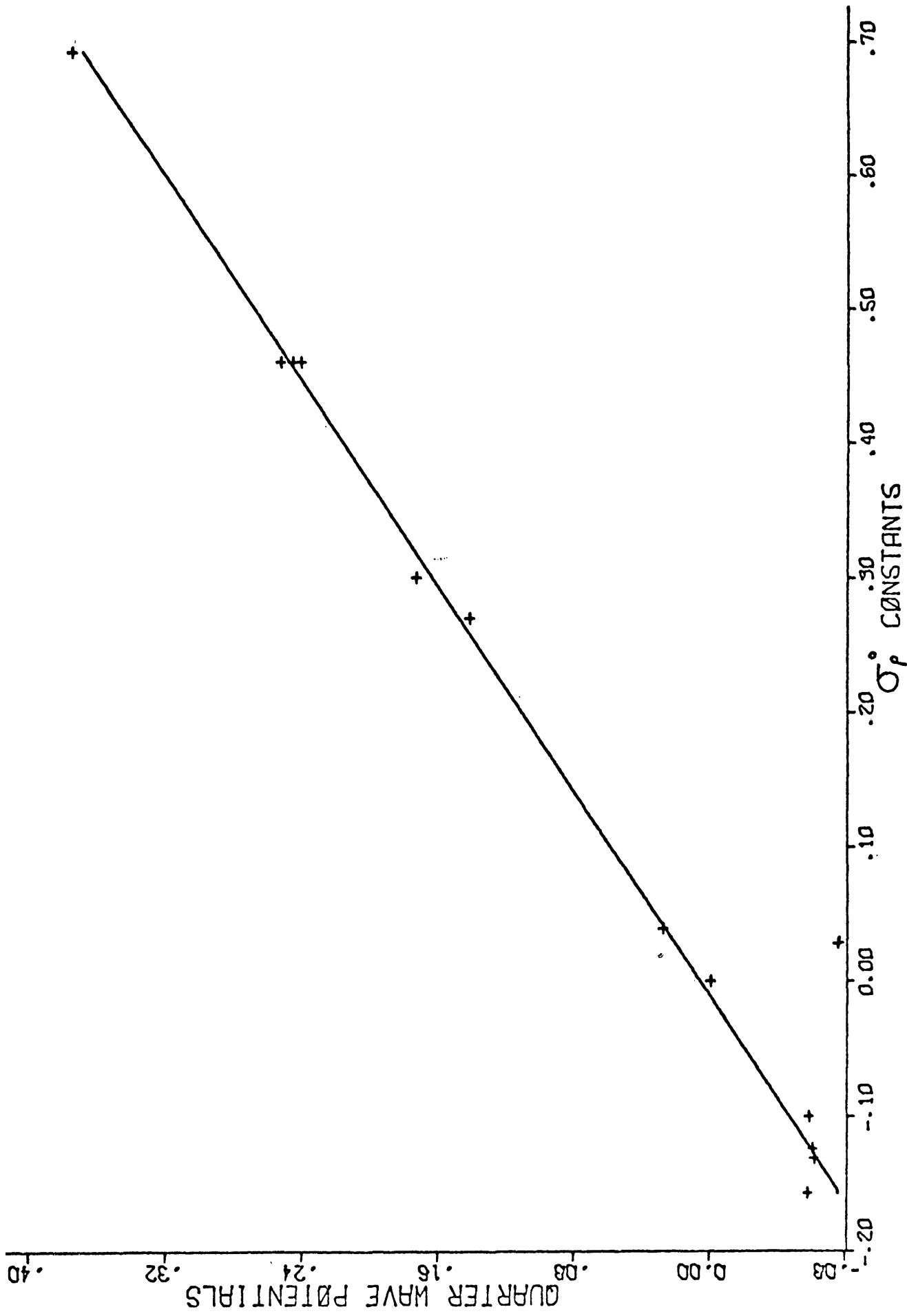


Figure 4. PLOT OF σ_p CONSTANTS VS THE QUARTER WAVE POTENTIALS

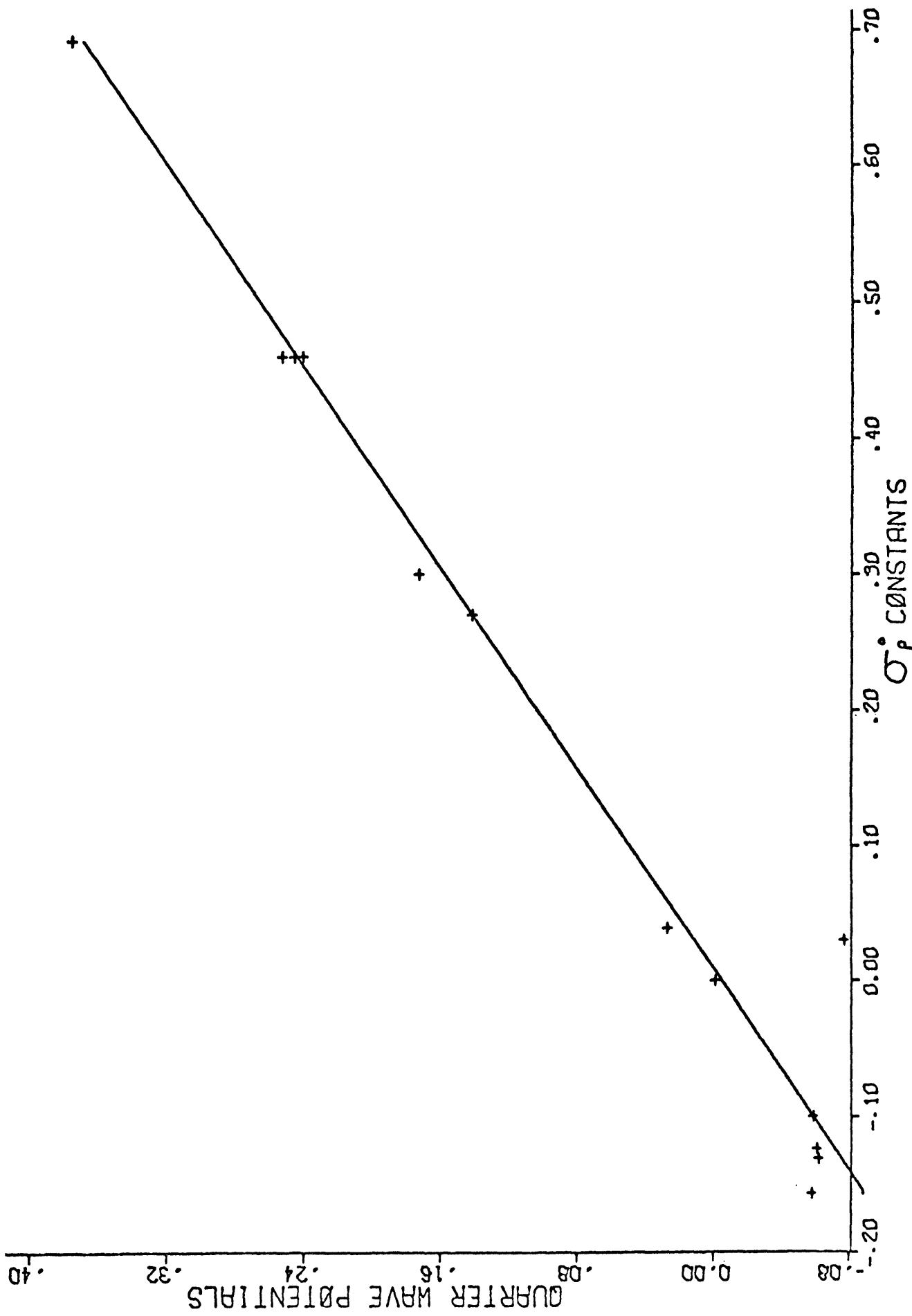


Figure 5. PLOT OF σ_p CONSTANTS VS THE QUARTER WAVE POTENTIALS

Table 2. Chronopotentiometric quarter wave potentials and corresponding σ_p° constants for monosubstituted ferrocenes.

<u>Compound</u>	σ_p°	$\Delta E_{1/4}^\circ$
Isopropylferrocene	-0.157 (a)	-0.057 (d)
Ethylferrocene	-0.131 (a)	-0.061 (d)
Methylferrocene	-0.124 (a)	-0.060 (d)
Methoxyferrocene	-0.100 (a)	-0.058 (e)
Acetamidoferrocene	+0.030 (b)	-0.076
Phenylferrocene	+0.039 (a)	+0.028 (d)
Iodoferrocene	+0.270 (c)	+0.142 (d)
Bromoferrocene	+0.300 (a)	+0.173
Carboethoxyferrocene	+0.460 (c)	+0.241 (d)
Carbomethoxyferrocene	+0.460 (c)	+0.246 (d)
Acetylferrocene	+0.460 (c)	+0.253
Cyanoferrocene	+0.690 (c)	+0.375 (e)
Ferrocene	0.000	0.000
(a) From reference (43)	(b) From reference (41)	
(c) From reference (42)	(d) From reference (14)	
(e) From reference (11)		

Table 3. Statistical evaluation of the correlation between the quarter wave potentials and the σ_p° constants.

<u>Computation No.</u>	<u>Compounds Listed in Table 2 Which Were Omitted</u>	<u>Slope of Regression Line</u>	<u>Correlation Coefficient</u>	<u>Standard Dev. ($\Delta E_{1/4}$)</u>
1	None	0.540	0.983	0.028
2	Acetamidoferrocene	0.527	0.998	0.008

The infrared spectra of ferricenium tetrachloroferrate (III), acetylferricenium tetrachloroferrate (III), acetamidoferricenium tetrachloroferrate (III), and 1-1'-dichloroferricenium tetrachloroferrate (III) were taken on KBr pellets (Figs. 6-9).

The ferricenium cation has been studied in detail in the infrared region by Pavlik and Klikorka (44). These workers reported the infrared spectra of ferricenium tetrachloroferrate, tetrabromoferrate, tetraiodomercurate, reineckate, molybdate, tungstosilicate, and picrate in nujol mulls in the 400-2200 cm^{-1} region and in hexachlorobutadiene in the 2800-4000 cm^{-1} region. A detailed analysis of the ferricenium cation was made, and assignments were made for many of the frequencies.

Table 4 lists the bands which were found in the spectrum of ferricenium tetrachloroferrate taken on KBr. Assignments of the bands were made from the data of Pavlik and Klikorka (44).

The region 300-400 cm^{-1} contains a very strong band which was present in the spectra of all the tetrachloroferrate (III) salts prepared. Pavlik and Klikorka (44) did not report a band for the ferricenium cation in this region. In addition, this band remained very nearly constant in position for all of the tetrachloroferrate (III) salts which were prepared. On the basis of these considerations, the band at 375 cm^{-1} was assigned to the tetrachloro-

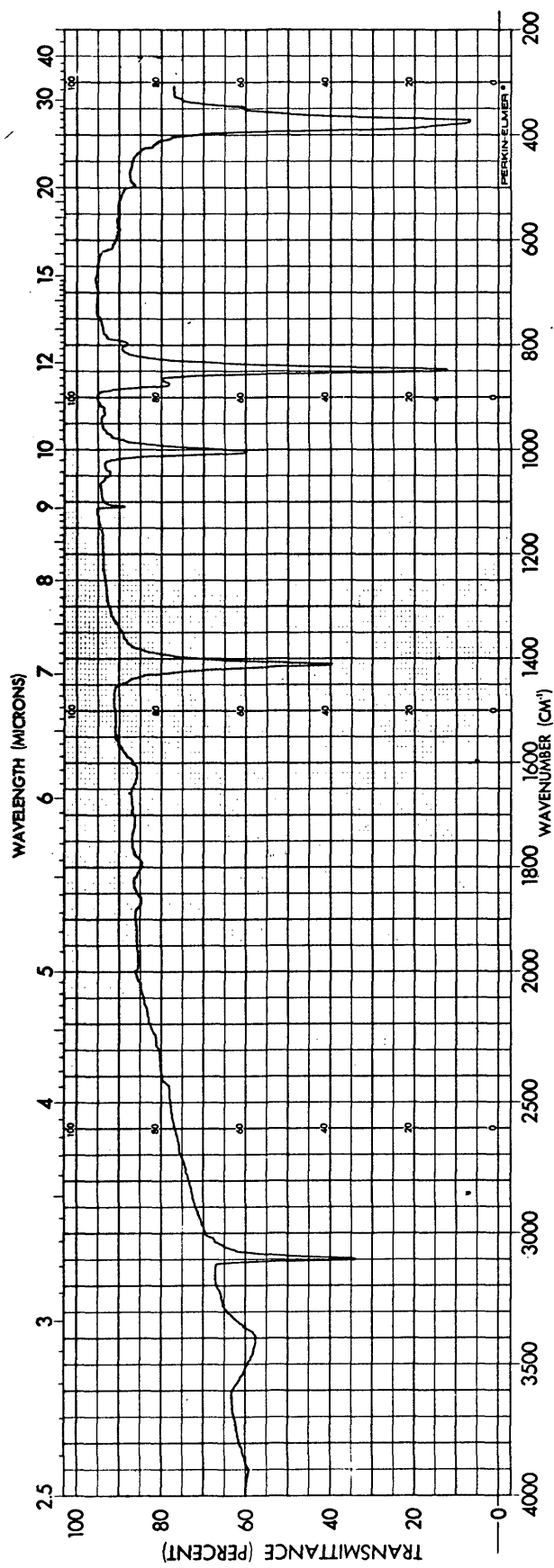


Figure 6. The infrared spectrum of ferricinium tetrachloroferrate (III) in KBr.

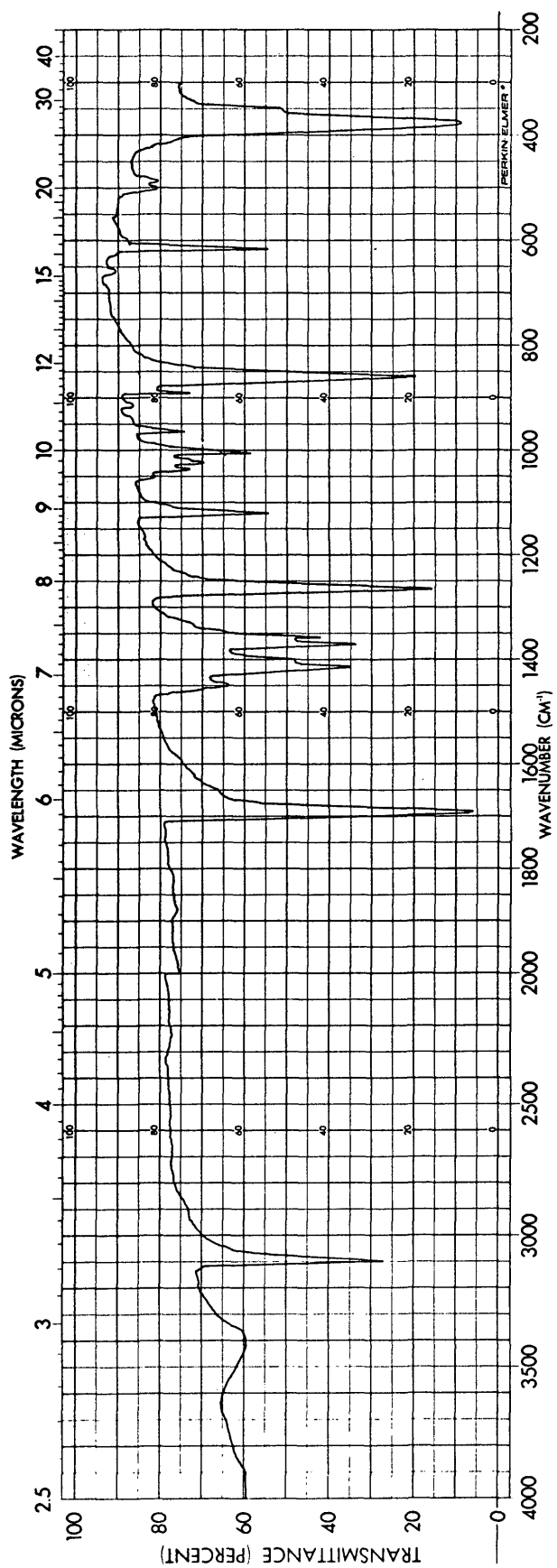


Figure 7. The infrared spectrum of acetylferricinium tetrachloroferrate (III) in KBr.

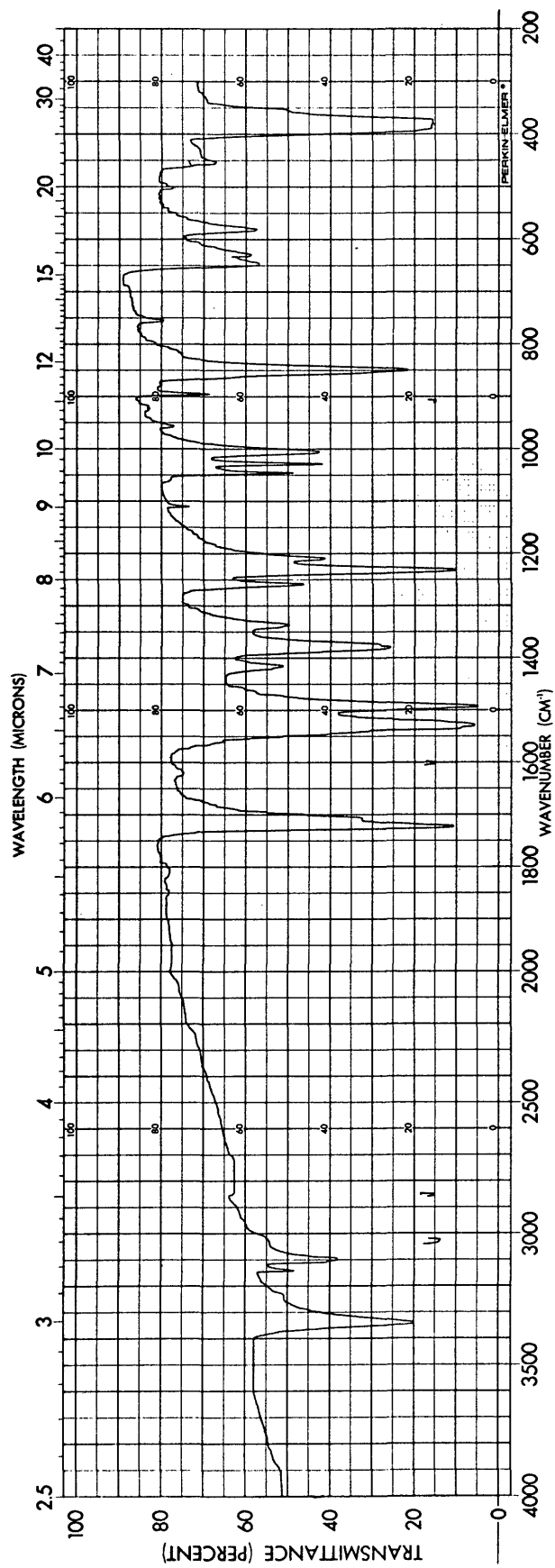


Figure 8. The infrared spectrum of acetamidoferricinium tetrachloroferrate (III) in KBr.

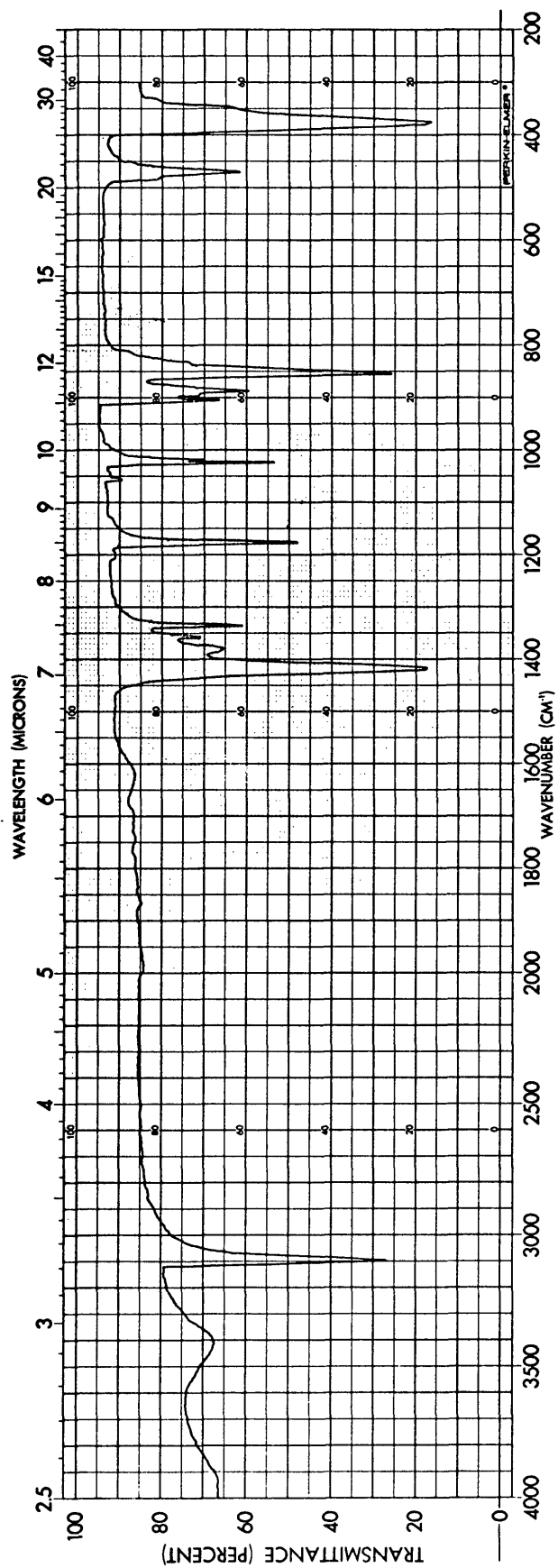


Figure 2. The infrared spectrum of 1-1'-dichloroferricenium tetrachloroferrate (III) in KBr.

<u>Frequency</u> (cm ⁻¹)	<u>Assignment</u>
3400 (w)	
3100 (s).....	C-H Stretching
1865 (w)	
1797 (w)	
1620 (w)	
1413 (s).....	Antisymmetric C-C Stretching
1111 (w).....	Antisymmetric Ring Breathing
1048 (w).....	C-H Bending (\perp)
1004 (ms).....	C-H Bending (//)
878 (w).....	Ring Distortion (//)
850 (s).....	C-H Bending (\perp)
800 (w)	
498 (w).....	Antisymmetric Ring Tilting
415 (sh).....	Antisymmetric Ring- Iron Stretching
375 (s)	
350 (sh)	

Table 4. Assignment of the infrared bands in the ferri-
cenium cation.

ferrate (III) anion (45).

Pavlik and Zizek (46) studied the tetrachloroferrate, reineckate, and tungstosilicate salts of the acetyl-ferricenium cation as nujol mulls. These workers centered their attention on the infrared bands in the 1690-1694 cm^{-1} and 1264-1268 cm^{-1} regions. The band in the 1690-1694 cm^{-1} region was assigned to the stretching frequency of the carbonyl C=O of the acetyl group. This band in acetylferrocene was reported to occur at 1683 cm^{-1} (nujol). There was, then, a shift of 7-11 cm^{-1} in the carbonyl stretching frequency toward higher energy when acetylferrocene was oxidized to the acetylferricenium cation. The band in the 1264-1268 cm^{-1} region was assigned to a complex combination of acetyl-ring interactions. This band was also observed to shift 7-11 cm^{-1} when acetylferrocene was oxidized, but the shift in this case was toward higher energy. The shifts observed in both of these bands were rationalized as an effect of greater conjugation of the acetyl group with the ferrocene nucleus in the acetylferricenium cation than in acetylferrocene.

The infrared data which were obtained for acetylferricenium tetrachloroferrate (III) in this study was in general agreement with that obtained by Pavlik and Zizek (46), but a much greater amount of detail was obtained in the spectrum. Table 5 lists the infrared bands for acetylferricenium tetrachloroferrate (III) which were

Infrared Bands Found in
the Present StudyInfrared Bands Found by
Pavlik and Zizek (46)

3420 (w)	
3095 (s)	
3000 (sh)	
1880 (vw)	
1691 (s).....	1690 (ms)
1650 (sh)	
1455 (sh)	
1449 (w)	
1429 (sh)	
1413 (ms).....	1418 (ms)
1401 (sh)	
1370 (ms)	
1356 (ms)	
1330 (sh).....	1330 (w)
1263 (s).....	1265 (ms)
	1182 (w)
	1149 (w)
1121 (ms).....	1121 (ms)
1052 (w)	
1036 (w)	
1023 (w)	
1003 (ms).....	1008 (w)
962 (w).....	967 (w)
938 (sh)	
913 (vw)	
885 (w).....	890 (sh)
861 (s).....	859 (ms)
839 (sh)	
	783 (ms)
750 (sh)	
	680 (w-b)
660 (vw)	
613 (ms)	
501 (w)	
486 (w)	
413 (sh).....	411 (sh)
375 (s)	
350 (sh)	

Table 5. Infrared spectral data for acetylferricenium
Tetrachloroferrate (III).

found in this study and those which were reported by Pavlik and Zizek (46).

The spectrum of acetylferrocene was taken in KBr so that the magnitude and direction of the band shifts observed by Pavlik and Zizek (46) could be checked. The results were compatible except for the magnitude of the shift of the carbonyl stretching frequency. The carbonyl band of acetylferrocene was observed at 1651 cm^{-1} in KBr, which indicates a shift of nearly 40 cm^{-1} toward higher energy for the ion. Raush and coworkers (47) reported the carbonyl stretching frequency of acetylferrocene at 1658 cm^{-1} in KBr.

Acetamidoferricenium tetrachloroferrate (III) and 1-1'-dichloroferricenium tetrachloroferrate (III) have not been previously reported.

Bands found for acetamidoferrocenium tetrachloroferrate (III) in KBr were 3340 (s) , 3240 (sh) , 3140 (w) , 3110 (sh) , 3100 (ms) , 3030 (ms) , 1850 (vw) , 1810 (vw) , 1721 (s) , 1705 (sh) , 1620 (vw) , 1535 (sh) , 1530 (sh) , 1492 (s) , 1465 (sh) , 1455 (sh) , 1421 (sh) , 1416 (ms) , 1380 (s) , 1375 (sh) , 1338 (ms) , 1260 (ms) , 1231 (s) , 1210 (ms) , 1110 (w) , 1046 (ms) , 1029 (ms) , 1006 (ms) , 958 (w) , 922 (vw) , 896 (w) , 850 (s) , 817 (sh) , 755 (w) , 648 (ms) , 581 (ms) , 501 (vw) , 453 (w) , 430 (sh) , 381 (s) , and 355 (sh) .

All of the characteristic infrared bands which were

assigned to the ferricenium cation were also present in the acetamidoferricenium cation. Table 6 lists the band assignments made for the ferricenium cation along with the corresponding bands in the spectrum of acetamidoferricenium tetrachloroferrate (III).

Table 7 lists the major amide bands in the infrared spectrum of acetamidoferricenium tetrachloroferrate (III) and compares them with the same bands found in acetamidoferrocene. Column 2 of Tab. 7 lists the infrared data for acetamidoferrocene in dilute acetonitrile solution, and column 3 of Tab. 7 lists the infrared data of acetamidoferrocene in KBr.

The assignments of the bands were those made by Bellamy (48) and Gerrard and coworkers (49). The amide I band represents the carbonyl stretching frequency of the ketonic form of the amide. Rigorous assignment of the amide II and III bands was, however, much more difficult. The bulk of the evidence indicated that both N-H and C-N motions are involved in the amide II band, but that the amide III band is due primarily to C-N motions.

Monosubstituted amides are known to undergo hydrogen bonding both in the solid state and in concentrated solution. Figure 10 represents the type of interaction which is involved in the formation of such a hydrogen bond. In the case of acetamidoferrocene, R_1 would represent the ferrocene nucleus and R a methyl group.

Table 6. Assignment of the characteristic ferricenium bands in the acetamido-ferricenium cation.

<u>Ferricenium Tetrachloroferrate (III)</u>	<u>Acetamidoferricenium Tetrachloroferrate (III)</u>	<u>Assignment</u>
3100 (s)	3100 (ms)	C-H Stretching
1413 (s)	1416 (ms)	Antisymmetric C-C Stretching
1111 (w)	1110 (w)	Antisymmetric Ring Breathing
1048 (w)	1046 (ms)	C-H Bending (\perp)
1004 (ms)	1006 (ms)	C-H Bending (\parallel)
878 (w)	879 (vw)	Ring Distortion (\parallel)
850 (s)	850 (s)	C-H Bending (\perp)
498 (w)	501 (vw)	Antisymmetric Ring Tilting
415 (sh)	425 (sh)	Antisymmetric Iron- Ring Stretching

Table 2. Assignment of the characteristic amide bands in acetamidoferrocene and the acetamidoferricenium cation.

<u>Acetamidoferricenium Tetrachloroferrate (III) in KBr</u>	<u>Acetamidoferrocene in Acetonitrile</u>	<u>Acetamidoferrocene in KBr</u>	<u>Assignment</u>
3340	3430	3250	N-H Stretching
1721	1681	1651	Amide I Band
1530	1526	1575	Amide II Band
1231	1231	1283	Amide III Band

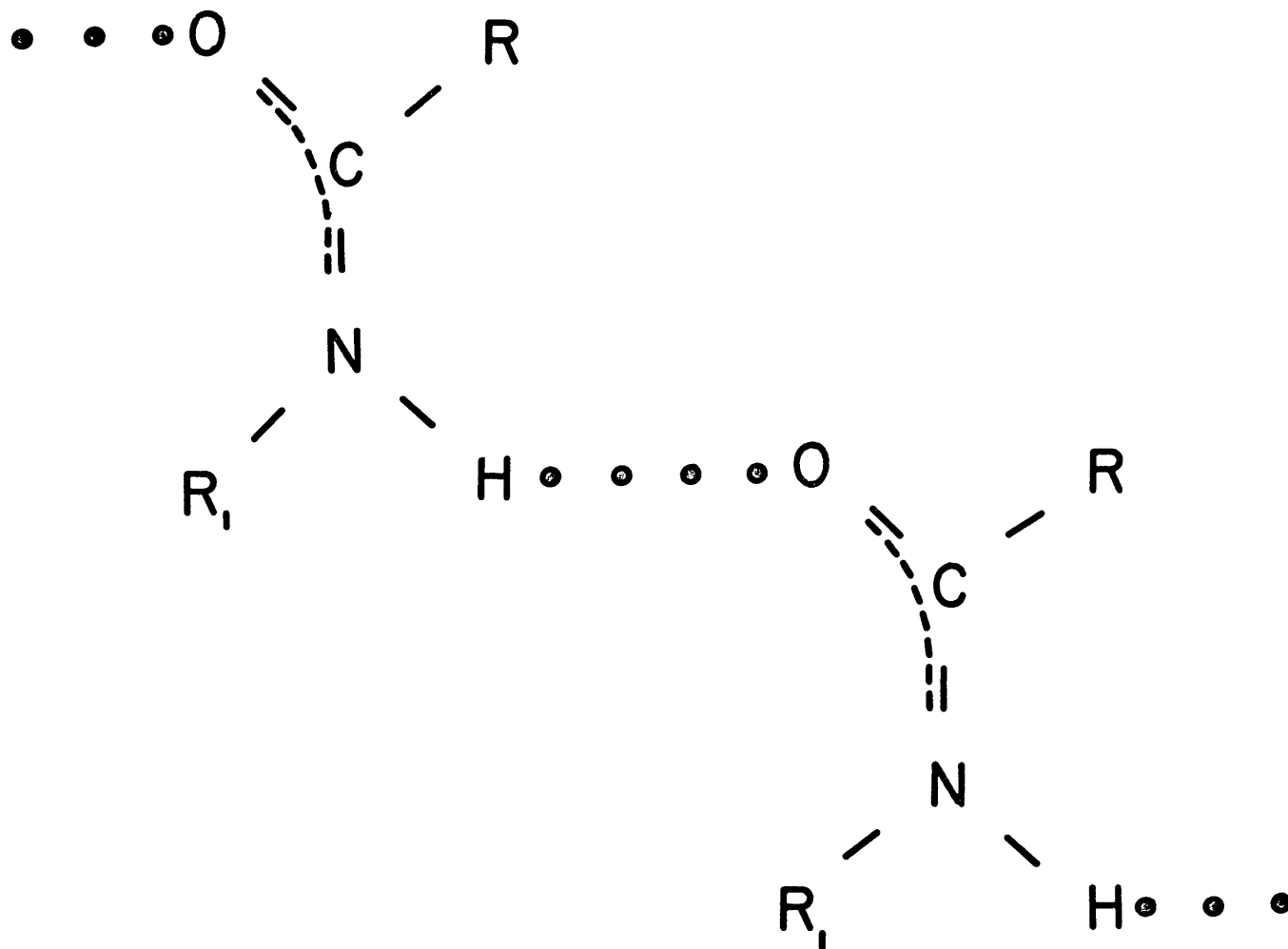


Figure 10. Hydrogen bonding between monosubstituted amides.

If hydrogen bonding takes place in monosubstituted amides, electron density in the carbonyl group is shifted more toward the oxygen atom as a result of the weak bond formed with the amide hydrogen of an adjacent molecule. The distribution of electron density in the π -system of the carbonyl group becomes much less evenly distributed, giving the double bond more ionic character. This increase in the ionic character of the carbonyl double bond causes a shift in its infrared stretching frequency toward lower energy. The partial positive charge on the carbonyl carbon atom becomes greater, causing a delocalization of the non-bonded electron pair on the nitrogen atom toward the carbonyl carbon atom to compensate for the increase in positive charge. As a result, the C-N bond acquires considerable double bond character. Increasing the strength of the C-N bond results in a shift of its infrared absorption toward higher energy. The delocalization of the nitrogen non-bonded pair causes the nitrogen atom to acquire some positive charge. This positive charge on nitrogen, coupled with the effect of the hydrogen bond cause the N-H bond to become more ionic, and the characteristic absorption is shifted toward lower energy.

Comparison of the spectral data for acetamidoferrocene in dilute acetonitrile solution and in KBr indicated that hydrogen bonding occurred when acetamidoferrocene was

pressed into a KBr pellet. The amide I band was shifted by 30 cm^{-1} toward lower energy in KBr, indicating that coordination through the oxygen atom of the carbonyl group had taken place. The amide II and III bands were shifted toward higher energy by 45 cm^{-1} and 52 cm^{-1} , respectively. This could be accounted for by the increased double bond character of the C-N bond. The shift of the N-H stretching frequency by 180 cm^{-1} toward lower energy was also consistent with hydrogen bonding, indicating a highly ionic N-H bond.

The above considerations are consistent with those of Gerard and coworkers (49). These workers recorded the spectra of a large number of amides in dilute solution and as nujol mulls. In all cases the N-H frequencies and the amide I bands were shifted toward lower energy and the amide II and III bands were shifted toward higher energy in nujol.

Much the same type of reasoning can be used to explain the spectral shifts which occur when a Lewis acid coordinates with the oxygen atom of a monosubstituted amide. There is again a donation of non-bonding electron pairs on the carbonyl oxygen atom toward an electron accepting center. This coordination shifts the electron density in the carbonyl bond toward the oxygen atom, causing spectral shifts similar to those observed for hydrogen bonding. It should be noted that the amide hydrogen does

not participate in the formation of the donor-acceptor complex (Fig. 11). The only force acting on the N-H bond is the partial positive charge on the nitrogen atom, created by the delocalization of the nitrogen non-bonded electron pair toward the carbonyl carbon atom. The N-H bond should acquire less ionic character than when hydrogen bonding occurs, and the shift toward lower energy of the characteristic absorption should be less.

Paul and coworkers (50) in 1966 recorded the spectra of a number of monosubstituted amides complexed with Lewis acids. Upon formation of a 1:1 complex, the amide I band was observed to shift toward lower energy, the magnitude depending on the strength of the Lewis acid. The amide III band was shifted significantly toward higher energy, while the amide II band was retained as a weak absorption shifted slightly toward higher energy. The N-H stretching frequency in many cases was not observed, but in those cases in which it was, moderate shifts toward lower energy were recorded. Somewhat different results were obtained when coordination through nitrogen took place.

Gerrard and coworkers (49) recorded the spectra of a large number of amides complexed with boron trichloride. The results demonstrated that when coordination through oxygen took place, the N-H stretching frequency and the amide I band were shifted toward lower energy, while the amide II and III bands were shifted toward higher energy.

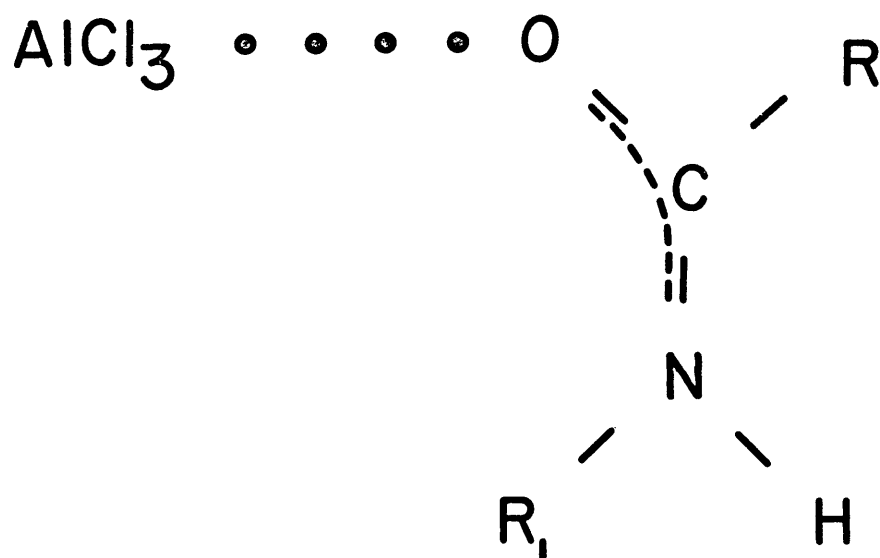


Figure 11. Formation of a Lewis acid complex with a mono-substituted amide.

Hall and Russell (11) proposed in 1967 that the unusually facile oxidation of acetamidoferrocene was a result of "internal solvation" of the positive iron atom in the acetamidoferricenium cation. It was postulated that in this type of interaction the non-bonded electron pairs on the carbonyl oxygen atom coordinated with the positive iron atom (see Fig. 2). If this type of interaction does take place, shifts in the infrared spectrum upon the oxidation of acetamidoferrocene to the acetamidoferricenium cation should parallel those observed for the formation of 1:1 complexes of monosubstituted amides with Lewis acids.

Infrared spectral data obtained for acetamidoferricenium tetrachloroferrate (III) in the present study do not indicate any interaction between the carbonyl oxygen atom and the iron atom in the acetamidoferricenium cation. Comparison of the spectral data for acetamidoferricenium tetrachloroferrate (III) in KBr with the data for acetamidoferrocene in dilute acetonitrile solution demonstrate that the spectral shifts are not compatible with those predicted from the spectra of 1:1 Lewis acid complexes of monosubstituted amides. The amide I band was shifted by 40 cm^{-1} toward higher energy, and the amide II and III bands remained essentially unchanged.

The increase in the carbonyl stretching frequency of acetamidoferricenium tetrachloroferrate (III) indicates that

no coordination is taking place through the oxygen atom of the carbonyl group. In addition, the unchanged positions of the amide II and III bands indicate no delocalization of the nitrogen non-bonded electron pair toward the carbonyl carbon atom.

The infrared spectral data provide evidence that the nitrogen non-bonded electron pair is interacting in some manner with the ferricenium nucleus, creating a large amount of positive charge on the nitrogen atom. This interaction could be either a resonance interaction with the cyclopentadienyl ring or a direct field interaction with the positive iron atom. Both types of interaction would cause a significant increase in the carbonyl stretching frequency.

No true resonance form can be drawn which would permit a direct interaction of the carbonyl π -electrons with the positive nitrogen atom. The positive charge on the nitrogen atom polarizes the C-N bond and in this manner exerts an inductive effect upon the π -electrons of the carbonyl group. The C-N bond would be expected to become more ionic, and the characteristic absorptions shifted toward lower energy. This is actually not the case, as the shift of the carbonyl π -electrons toward the carbonyl carbon atom compensates for the increased ionic nature of the C-N bond. The infrared spectral data obtained in the present study supports this conclusion, since there were no changes in

the positions of the amide II and III bands, which are directly influenced by the nature of the C-N bond.

Further evidence for the proposed interaction of the non-bonded electron pair on the nitrogen atom with the ferricenium nucleus was provided by the N-H stretching frequency. A positive charge on the nitrogen atom should cause the N-H bond to become more ionic. There is, however, no direct interaction of the amide hydrogen atom, such as in the formation of a hydrogen bond; therefore, the shift toward lower energy should be less than that observed when hydrogen bonding takes place. This was indeed the case; the N-H stretching frequency was shifted by 100 cm^{-1} toward lower energy as compared to 180 cm^{-1} when hydrogen bonding occurred.

Nyquist (51) in 1963 studied the infrared N-H and carbonyl stretching frequencies as a systematic function of para-substituents in acetanilide. His data support the conclusions which have been made concerning the electronic interactions which take place in the acetamido-ferricenium cation. Acetanilides substituted in the para-position with strongly electron withdrawing substituents showed a significant increase in the position of the carbonyl stretching frequency, while the N-H stretching frequency was decreased slightly with respect to acetanilide. These shifts were rationalized as an effect of the delocalization of the non-bonded nitrogen electron pair into the

benzene ring.

Acetamidoferricenium tetrachloroferrate (III) was found to have a spectrum in acetonitrile nearly identical with that in KBr. This eliminated any possibility that the observed spectral shifts were a result of solid state effects (49).

The bands found for 1-1'-dichloroferricenium tetrachloroferrate (III) were 3420 (w), 3100 (s), 1864 (vw), 1620 (vw), 1419 (s), 1382 (w), 1338 (ms), 1202 (vw), 1178 (ms), 1058 (vw), 1023 (ms), 1017 (w), 1004 (sh), 906 (w), 895 (sh), 889 (ms), 854 (s), 835 (sh), 485 (sh), 473 (ms), 378 (s), and 350 (sh). No attempt was made to interpret the spectrum of this compound, but the ferricenium structure was confirmed.

Visible Absorption Studies

Prins (52) in 1970 reported the visible spectral data for the ferricenium, 1-1'-dimethylferricenium, and acetyl-ferricenium cations. Table 8 summarizes this data.

The data in Tab. 8 demonstrate that substitution of methyl groups on the ferricenium cation caused a red shift of 28 $m\mu$ in the 617 $m\mu$ band, while the acetyl group caused a blue shift of 88 $m\mu$ in the 617 $m\mu$ band. This worker concluded from his data that the 617 $m\mu$ band was the result of a ligand to metal charge-transfer transition.

Rosenblum and coworkers (53) reported in 1964 the synthesis of a ferrocene-tetracyanoethylene charge-transfer

Table 8. Visible absorption data for ferricenium compounds obtained by Prins (53).

<u>Compound</u>	<u>Absorption</u> <u>(cm⁻¹)</u>	<u>Absorption Maximum</u> <u>(mμ)</u>	<u>Molar Extinction Coefficient</u>
Dimethylferricenium Cation	15,500	645	290
Ferricenium Cation	16,200	617	420
Acetylferricenium Cation	18,900	529	920

Table 2. Visible absorption data obtained for tetrachloroferrate (III) salts prepared in the present study.

<u>Compound</u>	<u>Absorption</u> <u>(mμ)</u>	<u>Molar Extinction Coefficient</u>
Ferricenium Tetrachloroferrate (III)	617	475
Acetylferricenium Tetrachloroferrate (III)	623	... (See text below)
Acetamidoferricenium Tetrachloroferrate (III)	730	514
1-1'-Dichloroferricenium Tetrachloroferrate (III)	698	415
Ethylferricenium Compound	621	420

complex. These workers were also able to prepare the same type of complex using several substituted ferrocenes. A good correlation was obtained when the energy of the charge-transfer band was plotted versus the chronopotentiometric quarter wave potentials for the substituted ferrocenes.

The data reported by Prins (52) suggested that the same type of correlation could be made between the energy of the 617 $m\mu$ absorption band of the ferricenium cations and the chronopotentiometric quarter wave potentials. Visible absorption spectra of ferricenium, acetylferricenium, acetamidoferricenium, and 1-1'-dichloroferricenium tetrachloroferrate (III) were taken in water. The visible and ultraviolet absorption spectra of ferricenium tetrachloroferrate (III) and acetamidoferricenium tetrachloroferrate (III) are presented in Figs. 12-15. The visible absorption spectrum of the ethylferricenium compound was also taken, even though the anion involved was not definitely identified. The data obtained are listed in Table 9.

Acetylferricenium tetrachloroferrate (III) was found to be very unstable in water. It appeared that the acetylferricenium cation was reduced to acetylferrocene, followed by a rapid degradation of the molecule. Attempts were made to obtain the absorption spectrum of acetylferrocenium tetrachloroferrate (III) in dichloromethane,

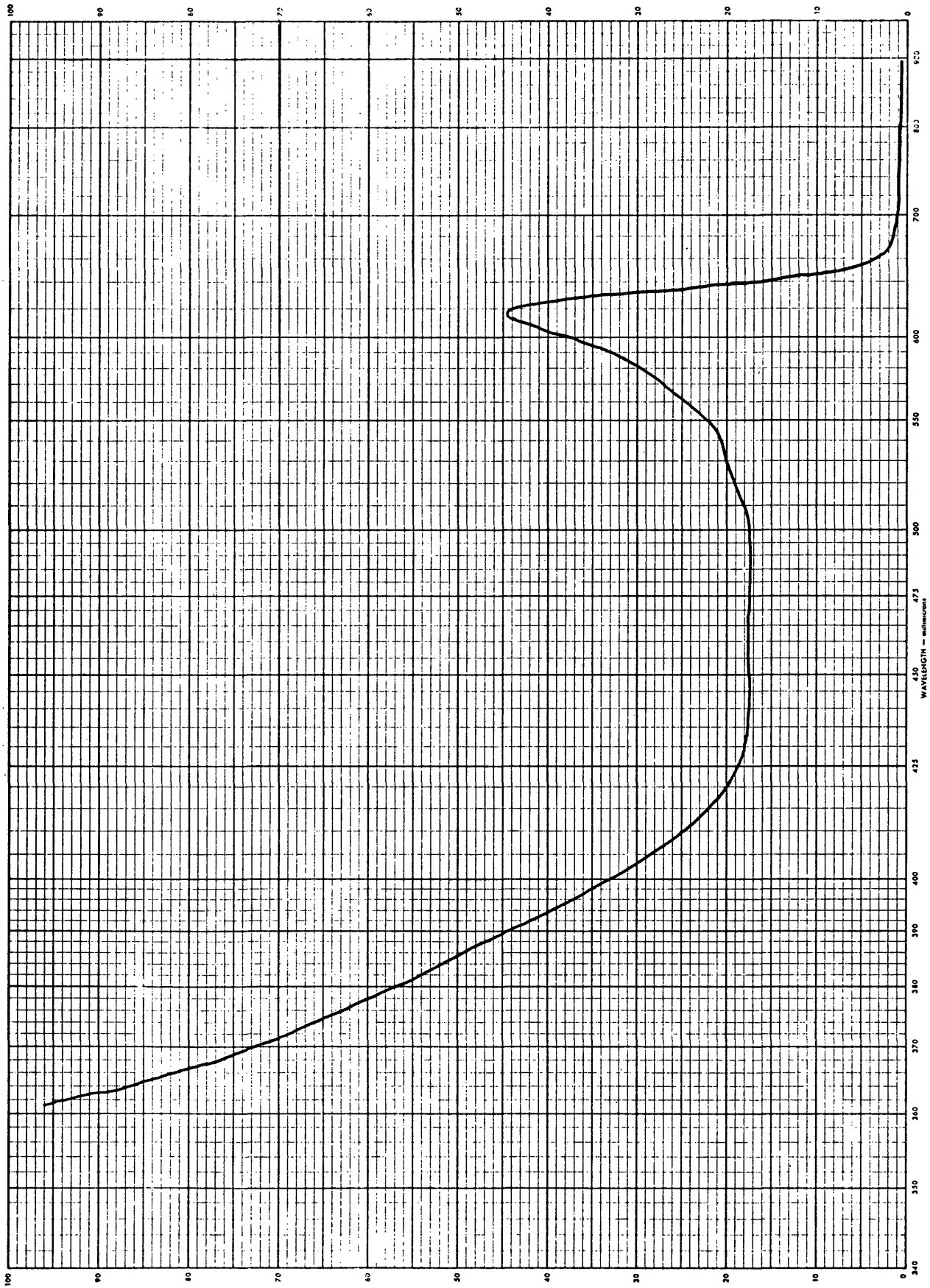


Figure 12. The visible absorption spectrum of ferricinium tetrachloroferrate (III).

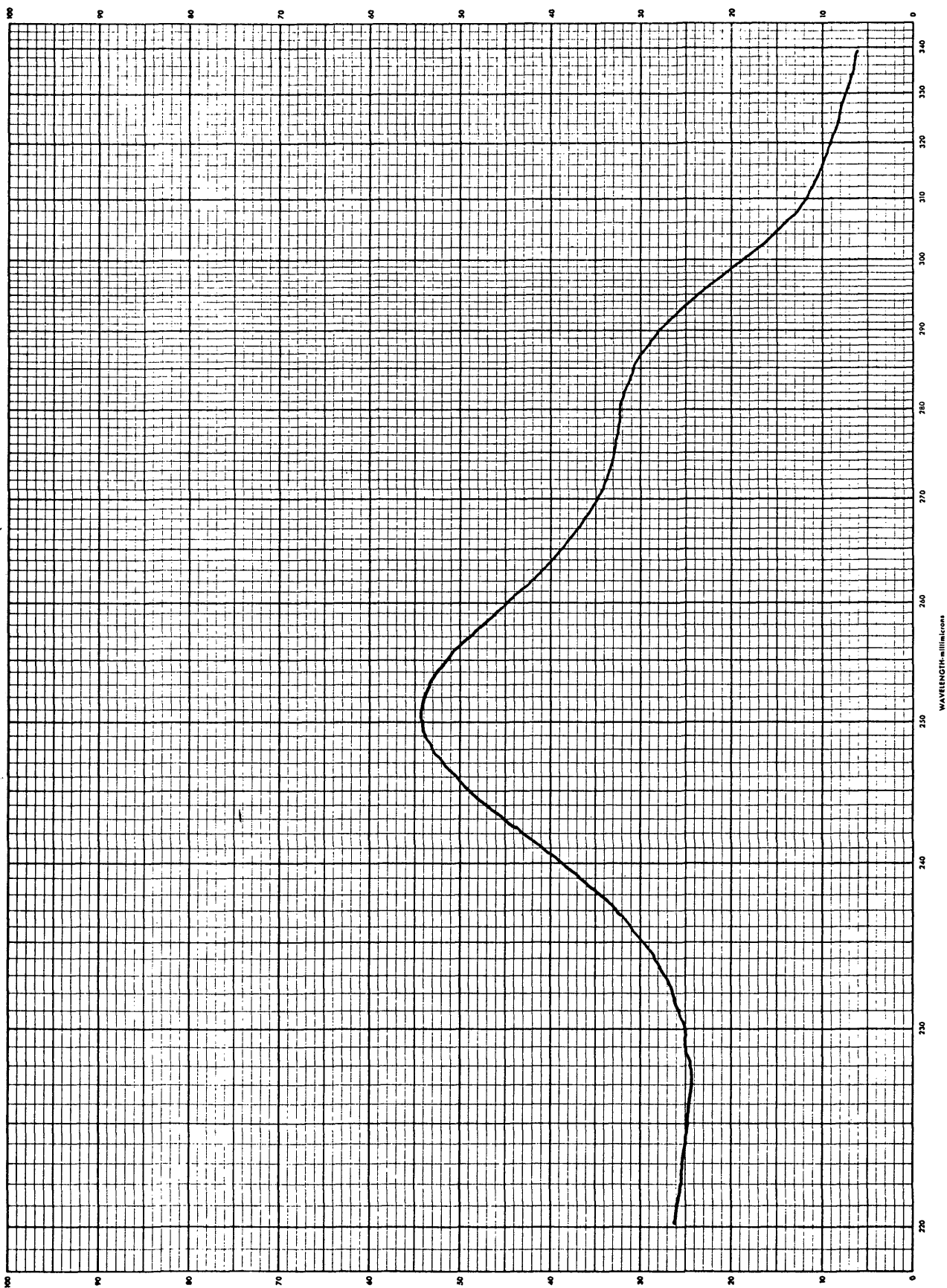


Figure 13. The ultraviolet absorption spectrum of ferricinium tetrachloroferrate (III).

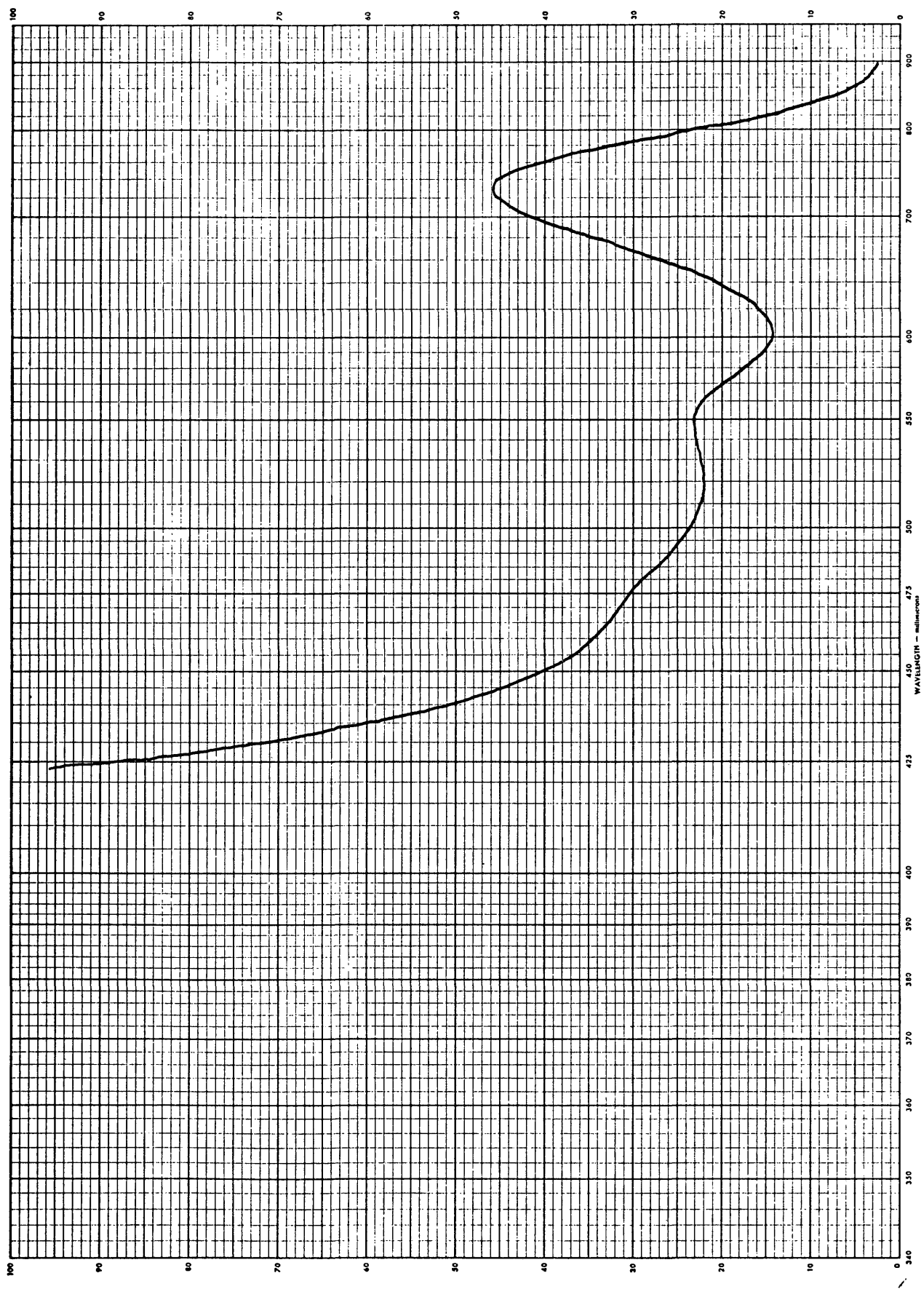


Figure 14. The visible absorption spectrum of acetamidoferricinium tetra-chloroferrate (III).

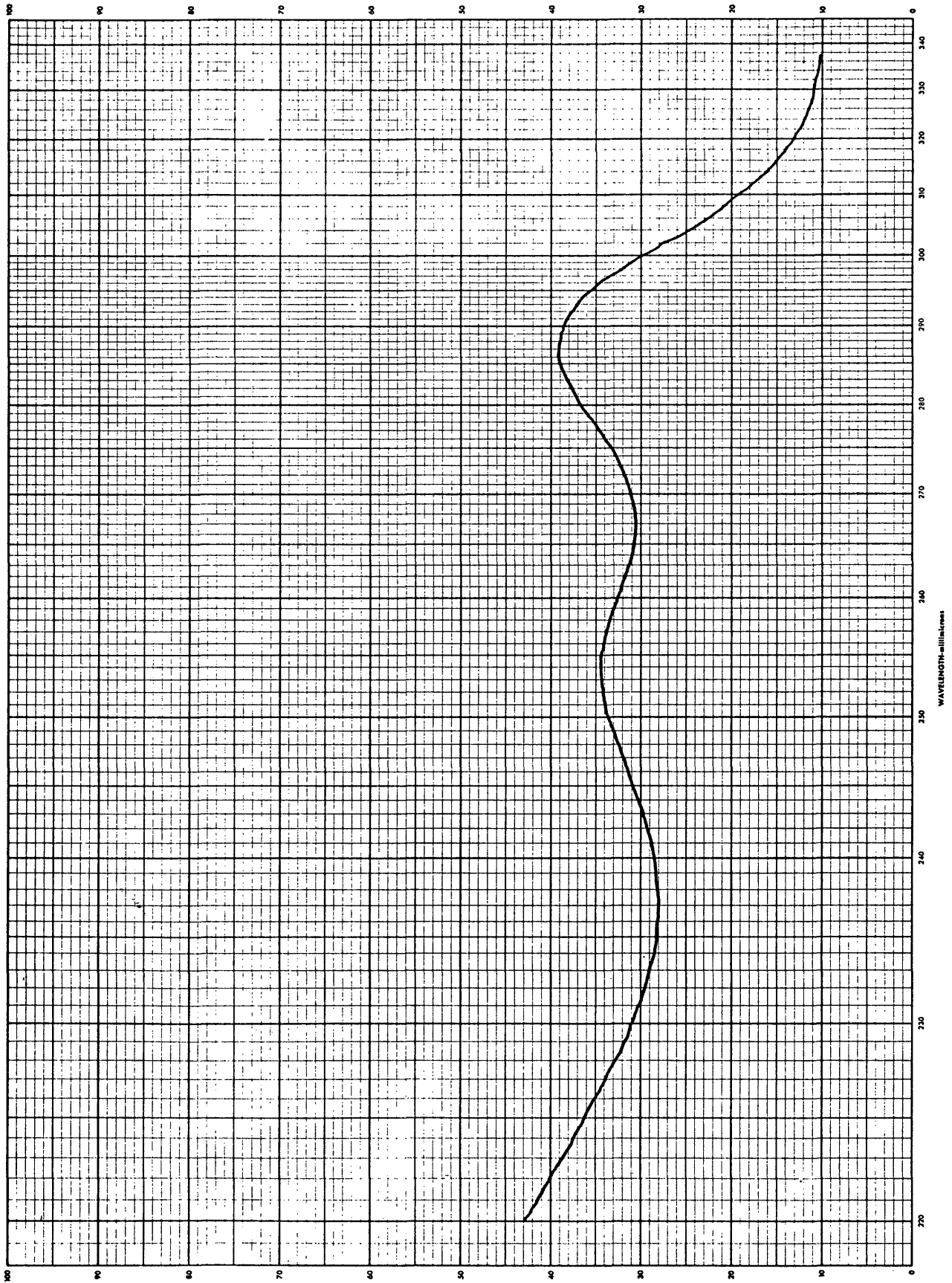


Figure 15. The ultraviolet absorption spectrum of acetamidoferric chloroferrate (III).

acetonitrile, and 1,2-dichloroethane, but rapid decomposition also took place in these solvents. As a result, the molar extinction coefficient for the absorption maximum of acetylferricenium tetrachloroferrate (III) could not be calculated.

Analysis of the results obtained in this study indicated that they were not consistent with the data and conclusions of Prins (52). The visible absorption maximum of the acetylferricenium cation showed a red shift of $6\text{ m}\mu$, as opposed to a blue shift of $88\text{ m}\mu$ which was reported by Prins (52). The 1-1'-dichloroferricenium cation would have been expected to show a blue shift, but a red shift of $81\text{ m}\mu$ was observed. The direction of the shift for the acetamidoferricenium cation was in the direction expected, but the magnitude of the shift indicated a much greater degree of electron donation than would have been expected for the acetamido group, based on reactions in the benzene series. The absorption band for the ethylferricenium cation was also shifted in the expected direction, but the magnitude of the shift was smaller than predicted by the results of Prins (52).

No explanation can be given at the present time for the disagreement between the two sets of data. It should be mentioned, however, that in his original communication, Prins (52) did not report the method of synthesis of his ferricenium salts, or even which anions were involved.

Later in 1970, Prins (54) published a paper which dealt with ESR studies on ferricenium cations. The experimental section indicated that a variety of oxidizing agents were used to produce the ferricenium cations, and that the ferricenium cations produced were never obtained in pure crystalline form.

Summary

1. Chronopotentiometric quarter wave potentials were determined for ferrocene, acetylferrocene, acetoxyferrocene, acetamidoferrocene, bromoferrocene, butylferrocene, and 1-1'-dichloroferrocene. The deviation of acetamidoferrocene from Hammett correlation plots reported by Hall and Russell in 1967 was verified.

2. Tetrachloroferrate (III) salts of ferrocene, acetylferrocene, acetamidoferrocene, and 1-1'-dichloroferrocene were prepared and characterized. Infrared spectroscopic studies demonstrated that coordination between the carbonyl oxygen atom and the positive iron atom does not take place in the acetamidoferricenium cation.

3. Visible absorption data collected for the tetrachloroferrate (III) salts did not agree with similar data reported by Prins in 1970. Prins had used his data to confirm molecular orbital calculations made for the ferrocene molecule.

BIBLIOGRAPHY

1. J. J. Kealy and P. L. Pauson, *Nature*, 168, 1039 (1951).
2. S. A. Miller, J. A. Tebboth, and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952).
3. G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Am. Chem. Soc.*, 74, 2125 (1952).
4. R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Am. Chem. Soc.*, 74, 3458 (1952).
5. K. Plesske, *Angew. Chem.*, 74, 301, 347 (1962).
6. M. Rosenblum, "Chemistry of the Iron Group Metallo-
cenes", John Wiley and Sons, New York, 1965.
7. A. N. Nesmeyanov and E. G. Perevalova, *Ann. N. Y. Acad. Sci.*, 67 (1965).
8. J. A. Page and G. Wilkinson, *J. Am. Chem. Soc.*, 74, 6149 (1952).
9. D. E. Publitz, G. Hoh, and T. Kuwana, *Chem. Ind.*, 635 (1959).
10. T. Kuwana, D. W. Publitz, and G. Hoh, *J. Am. Chem. Soc.*, 82, 5811 (1960).
11. D. W. Hall and C. D. Russell, *J. Am. Chem. Soc.*, 89, 2316 (1967).
12. D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 23, 420 (1958).
13. W. F. Little, C. N. Reilley, J. D. Johnson, and A. P. Sanders, *J. Am. Chem. Soc.*, 86, 1382 (1964).
14. W. F. Little, C. N. Reilley, J. D. Johnson, K. L. Lynn, and A. P. Sanders, *J. Am. Chem. Soc.*, 86, 1376 (1964).

15. H. C. Brown and G. Goldman, J. Am. Chem. Soc., 84, 1650 (1962).
16. L. M. Stock and F. W. Baker, J. Am. Chem. Soc., 84, 1664 (1962).
17. D. W. Hall and J. H. Richards, J. Org. Chem., 28, 1549 (1963).
18. J. Komenda and J. Tirouflet, Compt. Rend., 254, 3093 (1962)
19. G. Hoh, W. E. McEwen, and J. Kleinberg, J. Am. Chem. Soc., 83, 3949 (1961).
20. H. H. Jaffe, Chem. Revs., 53, 191 (1953).
21. R. W. Taft, Jr., "Steric Effects in Organic Chemistry", John Wiley and Sons, New York, 1956.
22. S. P. Gubin and E. G. Perevalova, Doklady Akad. SSSR, 143, 1351 (1962).
23. P. R. Wells, "Linear Free Energy Relationships", Academic Press, New York, 1968.
24. P. Delahay and T. Berzins, J. Am. Chem. Soc., 75, 2486 (1953).
25. P. Delahay, "New Instrumental Methods in Electro-Chemistry", Interscience, New York, 1954.
26. L. Gierst and A. Juliard, J. Phys. Chem., 57, 701 (1953).
27. C. N. Reilley, G. W. Everett, and R. H. Johns, Anal. Chem., 27, 483 (1955).
28. F. S. Arimoto and A. C. Haven, J. Am. Chem. Soc., 77, 6295 (1955).
29. G. A. Forcier and J. W. Olver, Anal. Chem., 37, 1447 (1965).
30. R. C. Weast, ed., "Handbook of Chemistry and Physics", Chemical Rubber Company, Cleveland, Ohio, 1966.
31. A. N. Nesmejanov, W. A. Ssasonowa, and V. D. Drosd, Chem. Ber., 93, 2717 (1960).
32. D. W. Hall, Ph. D. Thesis, California Institute of Technology, 1963.

33. R. W. Fish and M. Rosenblum, *J. Org. Chem.*, 30, 1253 (1965).
34. F. L. Headberg and H. Rosenberg, *J. Am. Chem. Soc.*, 92, 3239 (1970).
35. S. I. Goldberg, L. J. Kieth, and T. S. Prokopov, *J. Org. Chem.*, 28, 850 (1963).
36. R. F. Nystrom and C. R. A. Berger, *J. Am. Chem. Soc.*, 80, 2896 (1958).
37. A. N. Nesmejanov, E. G. Perevalova, and L. P. Jurjewa, *Chem. Ber.*, 93, 2730 (1960).
38. S. M. Aharoni and M. H. Litt, *J. Organometal. Chem.*, 22, 179 (1970).
39. D. W. Hall, E. A. Hill, and J. H. Richards, *J. Am. Chem. Soc.*, 90, 4972 (1968).
40. E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart, and Winston, New York, 1959.
41. R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Am. Chem. Soc.*, 81, 5352 (1959).
42. R. W. Taft, Jr., *J. Phys. Chem.*, 64, 1805 (1960).
43. Y. Yukawa, Y. Tsuno, and M. Sawasa, *Bull. Chem. Soc. Jap.*, 39, 2274 (1966).
44. I. Pavlik and J. Kilkorka, *Collect. Czechoslov. Chem. Commun.*, 30, 664 (1965).
45. R. J. H. Clark, *Spectrochim. Acta.*, 21, 955 (1965).
46. I. Pavlik and V. Zizek, *Collect. Czechoslov. Chem. Commun.*, 31, 1985 (1966).
47. M. D. Raush, E. O. Fischer, and H. Grubert, *J. Am. Chem. Soc.*, 82, 76 (1960).
48. L. J. Bellamy, "The Infrared Spectra of Complex Molecules", John Wiley and Sons, New York, 1958.
49. W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J. Chem. Soc.*, 2144 (1960).
50. R. C. Paul and B. R. Sreenathan, *J. Inorg. Nucl. Chem.*, 28, 1225 (1966).

51. R. A. Nyquist, *Spectrochim. Acta.*, 19, 1595 (1963).
52. R. Prins, *Chem. Comm.*, 280 (1970).
53. M. Rosenblum, R. W. Fish and C. Bennett, *J. Am. Chem. Soc.*, 86, 5166 (1964).
54. R. Prins, *Mol. Phys.* 19, 603 (1970).