[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY]

The Absorption Spectra of Ferric Compounds. I. The Ferric Chloride–Phenol Reaction

BY EDWARD F. WESP AND WALLACE R. BRODE

The production of a blue, violet or red coloration by the addition of ferric chloride to dilute solutions of phenols is a familiar reaction which has long been accepted as a qualitative test for this aromatic hydroxyl group.[1] Hantzsch and Desch[2] have demonstrated the necessity for the existence of a free hydroxyl group on the aromatic ring for the production of the color reaction. Possible structures for these colored complexes have been proposed by Raschig,[3] Weinland and Binder,[4] and Claasz.[5] Weinland and Binder isolated certain compounds from the reaction between ferric chloride and catechol which they characterized as the etherate of $Cl_2Fe\text{-}O\text{-}C_6H_4\text{-}OH$. They suggested that similar compounds are formed with other phenols and this type of structure has since been widely accepted as responsible for these colors. This explanation for the structure of the usual phenol–ferric chloride colored complex is not supported by data presented in this paper, although the structure for the guaiacol complex of Weinland and Binder may be quite correct for their isolated compound. This guaiacol compound is insoluble in water and differs in many other properties from the colored compounds obtained by the action of ferric chloride on nearly all of the other phenols which were tried.

In view of the difficulty experienced in attempts to isolate the colored complexes, a systematic study has been made of the absorption spectra of a number of phenols in various solvents and from these data it has been possible to predict with considerable certainty the nature of the colored complex.

Apparatus and Procedure

The observations recorded in the figures and table in this paper were made with a Bausch and Lomb spectrophotometer which was equipped with a modified DuBoscq colorimeter attachment, permitting the use of all glass cells and the rapid variation of cell thickness by changing the position of the glass plungers. The data are recorded in wave length values expressed in millimicrons (meters × 10^{-9}) as abscissa and in extinction coefficients, expressed as log I_0/I, as ordinates.[6] Measurements of the extinction coefficients were taken at intervals of 5 mμ from 430 to 720 mμ. In the case of certain very transient colors it was necessary to cool the absorption cell and to add glycerol to the colored solution to prevent its freezing. In the case of *o*-cresol the observations were made at −20°.

In all cases 5 cc. of 0.1, 0.01, or 0.001 *M* solution of the phenols was used to which from 0.1 to 0.5 cc. of 0.1 or 0.2 *M* ferric chloride was added. The amounts employed in each case, as well as the cell thickness, were so chosen that the value of the extinction coefficient was from 1.50 to 2.00 at the point of maximum absorption.

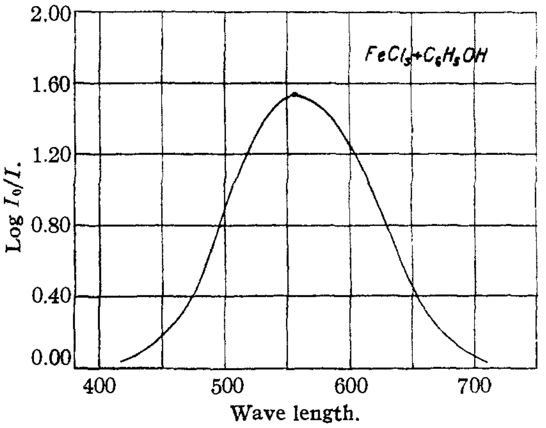

Fig. 1.—The absorption spectra of the colored complex produced by the interaction of phenol and ferric chloride in aqueous solution.

The absorption spectrum of the color produced by ferric chloride and phenol in water solution showed a simple, broad band with maximum absorption at 558 mμ (Fig. 1). This color and the colors produced by all other phenols followed Beer's law in moderate concentrations, although increase in concentration of either the iron salt or the phenol increased the intensity of the color.

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(1) (a) Runge, *Pogg. Ann.*, **31**, 65 (1834); *Z. prakt. Chem.*, **1**, 22 (1834); Schiff, *Ann.*, **159**, 164 (1871); Hesse, *ibid.*, **182**, 161 (1876).

(2) (b) Hantzsch and Desch, *ibid.*, **323**, 1 (1902).

(3) Raschig, *Z. anorg. Chem.*, **20**, 2065 (1907).

(4) Weinland and Binder, *Ber.*, **45**, 2498 (1912); *ibid.*, **46**, 874 (1913).

(5) Claasz, *Arch. Pharm.*, **253**, 360 (1915).

(6) For a more detailed discussion of the procedure of observation and the nature of the units of measurement see Brode, THIS JOURNAL, **51**, 1204 (1929); *Bureau Standards J. Res.*, **2**, 501 (1929).

If the formula of Weinland and Binder is correct, substitution of ferric bromide for ferric chloride should cause a shift of the region of absorption to longer wave lengths, because the weight of the absorbing molecule would be increased (an effect which has been previously shown with organic complexes of cobalt halides[7]). Ferric bromide, ferric nitrate, ferric sulfate and ferric ammonium alum all gave similar color reactions and the absorption curve in each case was identical in shape and position with that produced by using ferric chloride. It would thus appear that the negative portion of the iron salt takes no part in the production of the color.

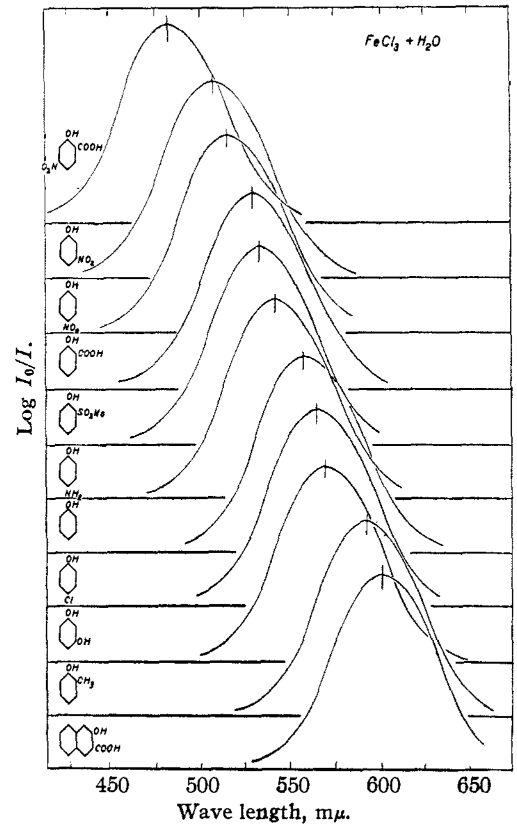

Fig. 2.—The absorption spectra of the colored complexes produced by the interaction of various phenols with ferric chloride in aqueous solutions.

Aqueous solutions of forty-four phenols and ten naphthols were treated with an aqueous solution of ferric chloride in order to determine the effect of substituents in the phenol upon the absorption spectra of the colors produced. In all cases the absorption curves were identical in shape with that obtained with phenol (Fig. 2). However, the position of the maximum and the intensity of the absorption varied as the phenolic compound was changed (Table I). Those phenols in which were substituted $-CH_3$, $-OH$, $-NH_2$ or halogen produced colors which were purple to blue in shade, the position of their maximum absorption being between 540 mμ and 600 mμ. Phenols containing these groups in the ortho or para position to the hydroxyl group produced colors which were quite unstable. This fading was accompanied by reduction of the ferric salt and the formation of a dark resinous substance which probably was due to the oxidation of the phenols. These same substituents when in the meta position produced much more stable colors; presumably because such substances are more resistant to oxidation or quinoid formation. Phenols containing substituents such as $-COOH$, $-CHO$, $-COOR$, $-NO_2$ or $-SO_3H$ produced very stable colors which were purple to red in shade. The maxima for these colors were always between 500 mμ and 535 mμ (Table I).

o-Chloro-, *o*-bromo- and *o*-iodophenols all produce absorption bands with maxima at the same wave length. If the phenolic compound were an integral part of the chromophore group the progressive increase in the molecular weight should cause a corresponding shift of the region of maximum absorption.[6,8] It appears that while the electrical nature of the phenol may greatly influence the wave length of the light selectively absorbed, it is not a definite part of the absorbing center.

Solvent Effect

With salicylic acid as a typical phenol and ferric chloride as the source of the ferric ions, the color reaction was tried in forty-eight solvents. Those solvents which may be considered to be derivatives of water or ammonia permitted the reaction to take place, and colors were produced. Those solvents which were hydrocarbons or their halogen substituents did not permit the production of color. Those solvents in which colors were produced are given in Table II. Those which did not permit color formation were: ethyl bromide, propyl bromide, ethylene chloride, trichloroethane, pentachloroethane, chloroform, carbon tetrachloride, carbon disulfide, ligroin, benzene, toluene, xylene, nitrobenzene, glacial acetic acid, ethylene, chlorohydrin and paraldehyde.

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(7) Brode, THIS JOURNAL, **53**, 2457 (1931); *Proc. Roy. Soc.* (London), **A118**, 286 (1928); **A120**, 21 (1928).

(8) Brode, *Ber.*, **61**, 1722 (1928).

The colors produced by ferric chloride and salicylic acid were specific for a given solvent, that in methyl alcohol being blue-purple, and that in quinoline being red. However, in all cases, irrespective of the nature of the solvents, the absorption curves were found to be identical in shape, and to have the simple symmetrical structure of a single band (Fig. 3). The differences in color observed are due to the change of the position of this absorption band under the influence of the solvent (Table II).

No relation was observed between the position of the region of maximum absorption and the physical properties of the solvents such as their dielectric constant, refractive index, or molecular volume, other than the regular variation in the

TABLE I

FERRIC IRON–PHENOL AND NAPHTHOL COLORS

Phenolic compound	Max. mμ	Relative intensity	Color	Stability	Temp. of obs., °C.
Phenol	558	10	Blue-purple	Unstable	0
o-Cresol	590	6	Blue	Unstable	−20
m-Cresol	555	7	Red-purple	Stable	25
p-Cresol	575	4	Blue	Unstable	0
o-Chlorophenol	570	10	Blue	Unstable	0
m-Chlorophenol	540	10	Red-purple	Stable	25
p-Chlorophenol	565	11	Blue	Unstable	0
2,4-Dichlorophenol	565	8	Blue	Unstable	0
o-Bromophenol	570	11	Blue	Unstable	0
m-Bromophenol	540		Red-purple	Stable	25
p-Bromophenol	565	11	Blue	Unstable	0
o-Iodophenol	570	7	Blue	Unstable	0
o-Aminophenol	(Ppt.)				
m-Aminophenol	U. V.		Orange		
p-Aminophenol	540	35	Red-purple	Unstable	0
o-Hydroxybenzoic acid	530	30	Red-purple		25
m-Hydroxybenzoic acid	U. V.				
p-Hydroxybenzoic acid	U. V.				
Salicylaldehyde	533	20	Red-purple	Stable	25
Salicylaldoxime	530	30	Red	Stable	25
Methyl salicylate	533	16	Red-purple	Stable	25
Ethyl salicylate	530	2	Red-purple	Stable	25
Phenyl salicylate	525	3	Red-purple	Stable	25
Sodium salicylate	530	35	Red-purple	Stable	25
5-Nitrosalicylic acid (40% alc.)	480	57	Red	Stable	25
6-Nitrosalicylic acid (95% alc.)	480	35	Red	Stable	25
4,6-Dinitrosalicylic acid (95% alc.)	U. V.		Amber	Stable	25
4-Sulfonalide of salicylic acid (95% alc.)	480	100	Red	Stable	25
3,5-Dibromosalicylic acid (40% alc.)	530	38	Red-purple		25
o-Nitrophenol	U. V.		Amber	Stable	25
m-Nitrophenol	505	2	Red	Stable	25
p-Nitrophenol	515	3	Red	Stable	25
Na salt of *p*-nitrophenol	512	3	Red	Stable	25
2,4-Dinitrophenol	U. V.		Red	Stable	25
o-Phenol Ba sulfonate	535	26	Red-purple	Stable	25
m-Phenol Ba sulfonate	505		Red	Stable	25
p-Phenol Ba sulfonate	535	29	Red-purple	Stable	25
p-Phenol Na sulfonate	535	15	Red-purple	Stable	25
Benzene azosalicylic acid (alc.)	505	25	Brown	Stable	25
Pyrocatechol (water)	U. V.				
Pyrocatechol (abs. alc.)	685	10	Blue	Stable	25
Resorcinol	570	12	Blue	Unstable	0
Hydroquinone			Blue	Unstable, oxidizes	
Pyrogallol (water)	U. V.				
Pyrogallol (abs. alc.)	Far red		Green-blue	Unstable	
Phloroglucinol	570	13		Unstable	0
Guaiacol (water)	U. V.				
Guaiacol (abs. alc.)	650	5	Blue	Stable	25

TABLE I (*Concluded*)

Phenolic compound	Max. mμ	Relative intensity	Color	Stability	Temp. of obs., °C.
Thiosalicylic acid (ether)	580	14	Blue	Unstable	0
Thiophenol (ether)			Blue-green	Unstable	
Acetoacetic ester	513	15	Red	Stable	25
1-Naphthol-2-sulfonic acid	575–580 (Gen. Abs.)	4	Green	Unstable	0
1-Naphthol-4-sulfonic acid	595–600 (530–540)*	14	Blue-purple	Unstable	0
1-Naphthol-5-sulfonic acid	530–540 (575–580)*	7	Purple-blue	Unstable	0
1-Naphthol-3,6,8-trisulfonic acid	610	46	Blue	Stable	25
2-Naphthol-7-sulfonic acid	590–600	6	Blue	Unstable	0
2-Naphthol-6-sulfonic acid	595	8	Blue	Unstable	0
2-Naphthol-6,8-disulfonic acid	590–595	8	Blue	Stable	25
2-Naphthol-3,6-disulfonic acid	590–595	7	Blue	Unstable	0
2-Hydroxy-3-naphthamide	600	300	Blue	Stable	25

*Band shifts to this position.

TABLE II

THE EFFECT OF SOLVENTS ON THE FERRIC IRON–PHENOL COLORS

(0.1 cc.–0.3 mole $FeCl_3$, 5.0 cc.–0.1 mole salicylic acid)

Solvent	Max. mμ	− log ε (0.5 cm. cell)	Color	Color of $FeCl_3$ solution	Solvent properties Dielectric constant	Solvent properties Refrac. index d_4
Water	530	3.00	Red-purple	Yellow	81.97	1.3329
Methyl alcohol	558	2.32	Blue-purple	Yellow	33.7	0.7980
Ethyl alcohol	548	2.17	Purple	Yellow	25.7	.7917
n-Propyl alcohol	540	1.75	Red-purple	Yellow	21.8	.8044
n-Butyl alcohol	538	1.27	Red-purple	Yellow	17.8	.8099
i-Butyl alcohol	536	1.28	Red-purple	Yellow	18.7	.8046
n-Amyl alcohol	538	1.26	Red-purple	Yellow	15.8	.8142
i-Amyl alcohol	538	1.30	Red-purple	Yellow	15.3	.8134
n-Hexyl alcohol	540	0.81	Red-purple	Yellow		
i-Hexyl alcohol	538	.85	Red-purple	Yellow		
s-Propyl alcohol	505	.66	Red	Dark brown	26.0	.7887
s-Butyl alcohol	515	.53	Red	Dark brown	15.5	
s-Amyl alcohol	505	.48	Red	Dark brown		
t-Butyl alcohol	480–490	.40	Red	Dark brown	11.4	.7864
t-Amyl alcohol	480		Red	Dark brown	11.7	
Cyclohexanol	480	.70	Red	Yellow	15.0	.9463
Methyl acetate	515–526	.39	Red	Yellow	7.2	.9244
Ethyl acetate	510–520	.40	Red	Yellow	6.0	.8946
n-Butyl acetate	510–520	.15	Red	Yellow	5.1	
Acetone	540	.94	Red-purple	Yellow	21.3	.7911
Acetophenone	520	.26	Red	Brown	18.3	1.0293
Ethyl ether	U. V.		Orange-red	Yellow	4.33	0.7183
Furfuraldehyde	U. V.		Amber	Brown-yellow	41.9	1.1594
Aniline	440–450		Red	Dark red-brown	7.21	1.0216
Dimethylaniline	450–460	2.30	Red	Dark red-brown	4.4	0.9575
Pyridine			Red	Dark red-brown	12.0	.9808
Quinoline	440	4.12	Red	Dark red-brown		1.0895
Liquid ammonia			Red	Dark red-brown		

case of homologous compounds attributable to slight difference in molecular weight. This is entirely in accord with previous work.[9] In the series of primary aliphatic alcohols the color formed in methyl alcohol is blue-purple and the absorption maximum is at 558 mμ. As the higher homologs are used the color becomes more red and the maximum shifts progressively toward the blue until 538 mμ is reached in the primary butyl alcohols, after which the region of maximum absorption is nearly constant. Secondary alcohols cause a shift in the position of maximum absorption to the region of 505 mμ. The tertiary alcohols caused absorption at about 480 mμ.

A very close relation is shown between the dielectric constant of the solvent and the intensity of the color produced. Those solvents which have

[9] Brode, *J. Phys. Chem.*, **30**, 56 (1926).

a high dielectric constant produce intense absorption. Traube[10] noted that the color produced by acetoacetic ester and ferric chloride is more intense the more associated is the solvent. Work in progress has shown that the colors developed by phenols and by acetoacetic ester derivatives with ferric salts are essentially similar.

Although the solvent apparently forms no part of the colored compound the reaction has been shown to proceed only in those solvents which are derivatives of water or ammonia.

As a part of the proof of the existence of $Fe(CNS)_6^{\equiv}$ as the colored complex in solutions of ferric thiocyanate,[11] it has been shown by means of electrolysis that the complex is a negative ion. Electrolysis of the phenol–ferric iron complex has shown an analogous reaction to the above with a marked increase in the intensity of the color at the anode as compared with the color intensity at the cathode.

Theoretical

While it has not been possible to isolate the unstable complex ion responsible for the color in the ferric chloride–phenol solution, nevertheless certain facts concerning this reaction have been established and in the light of these, a mechanism is proposed. These facts briefly are: (1) those substances essential to the color reaction are (a) ferric ions, (b) a mildly acidic –OH or –SH group such as occurs in phenols, thiophenols and enolic forms of tautomeric substances and (c) a solvent capable of coördination. (2) The colored complex is a negative ion, as evidenced by the migration of the color to the anode under an applied potential. (3) Change in the nature of the phenol or solvent may produce a change in the characteristic frequency of light absorbed and in the intensity of absorption. In all cases the shapes of the absorption curves are identical. (4) The color is destroyed by the addition of acids or bases.

It is quite generally accepted that the many compounds formed by the so-called transition elements such as iron, copper, vanadium, etc., are colored due to complex coördinated ions with the transition element as the central atom of the complex.

In the case of the ferric chloride–phenol color reaction it is suggested that the color is due to the formation of complex coördinated ions of the type $Fe(OR)_6^{---}$, wherein OR represents the ionized phenol. The color of such a complex ion would be due to the selective absorption of light by the iron atom. The energy state of this atom would be influenced by the nature of the surrounding atoms or molecules, which would be determined partially by the phenolic residues coördinated to the ferric ion and partially by the solvent present. According to this view, the general character of the absorption curves of ferric-phenol complexes would be the same since the absorption center or chromophore lies within the iron atom; however, since the nature of the phenol would contribute to the influences about the absorbing electrons, we should expect the frequency of the maximum absorption to be characteristic for a given phenol. The data are in accord with these views, which are further confirmed by the fact that the more pronounced the electrical nature of a phenolic group, the more effect it has upon the position of the maximum.

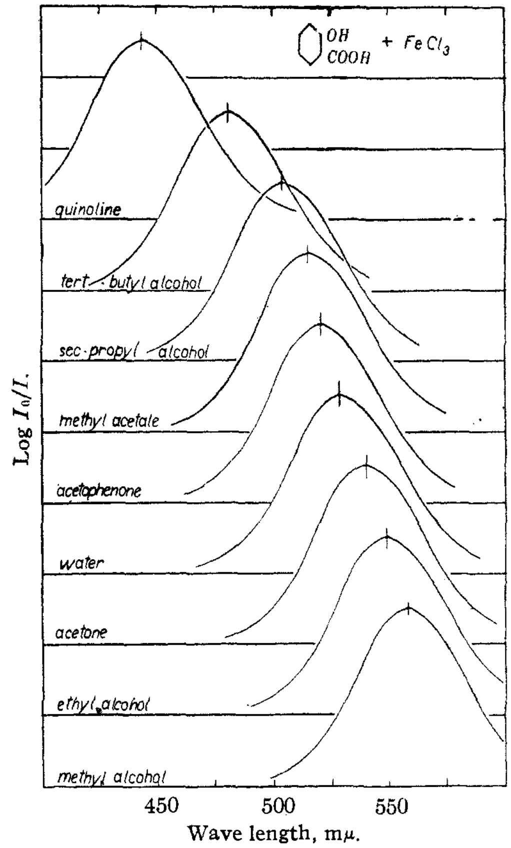

Fig. 3.—The influence of various solvents on the absorption spectra of the colored complex produced by the interaction of salicylic acid and ferric chloride.

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[10] Traube, *Ber.*, **29**, 1717 (1896); *ibid.*, **65**, 187 (1932); *ibid.*, **66**, 1545 (1933).

[11] Schlesinger and Van Valkenburgh, THIS JOURNAL, **53**, 1212 (1931).

It has been noted that the color is more intense in those solvents which are most highly associated, or, in the light of this proposed mechanism, in those solvents which will permit the ionization of the phenol to the greatest extent. This would build up the concentration of the RO^- ion and thus favor the formation of the complex. The electronic character of the solvent would aid in determining the fields of force surrounding the absorbing center and thus affect the characteristic frequency of light absorbed by a given complex.

Further support of the proposed colored ion is found in the coördinated complexes of ferric ion with the anions of weak acids, for example $Fe(CN)_6^{---}$ and $Fe(CNS)_6^{---}$. The absorption spectrum of $Fe(CNS)_6^{---}$ shows a simple band with maximum absorption at 490 mμ.[12] In ether solution this same compound shows a violet color with the maximum at 516 mμ of absorption.[13] Such absorption spectra are nearly identical in type with those of the ferric iron–phenol colors and hence it may be assumed that the cause of the color in both cases is very similar.

The existence of other complex ferric ions[14] has been demonstrated and they have been shown to correspond in structure and properties to the indicated phenol–ferric ion complex.

Summary

1. The absorption spectra of the colors produced by phenol and a number of ferric salts in aqueous solution have been measured and found to be identical in shape and position but not in intensity.

2. The absorption spectra of the colors produced by ferric chloride with forty-four phenols and ten naphthols in water solution have been measured and found to be identical in shape in all cases, but to differ in intensity and position as the nature and position of the groups substituted on the phenol are varied.

3. The behavior of salicylic acid with ferric chloride in forty-eight solvents has been studied. It was determined that color was produced only in those solvents which are derivatives of water or ammonia. In those cases where colors were produced (thirty-one solvents), the absorption bands were measured and were found to be identical in shape in all cases, but to vary in position and intensity with the nature of the solvent.

4. The color produced by the salicylic acid with ferric chloride was found to migrate to the anode during electrolysis, demonstrating that the colored body is negatively charged.

5. It has been postulated that the ferric iron–phenol colors are due to the formation of complex coördinated negative ions of the type $Fe(OR)_6^{---}$.

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(12) Von Halban and Zimpelmann, *Z. Elektrochem.*, **34**, 387 (1928).

(13) Kayser, "Handbuch der Spektroscopie," 1905, Vol. III, p. 413.

(14) Weinland, "Einführung in die Chemie der Komplex-Verbindungen," Ferdinand Enke, Stuttgart, 1924, p. 143.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of Formic Acid from 0 to 60°[1]

BY HERBERT S. HARNED AND NORRIS D. EMBREE

The ionization constant of formic acid at 25° has been determined from measurements of cells without liquid junction by Harned and Owen.[2] They employed cells containing the weak acid in sodium chloride solutions, namely

$$H_2 \mid HAc\ (M), NaCl\ (m) \mid AgCl \mid Ag \mid AgCl \mid HCl\ (0.01) \mid H_2$$

For the purpose of testing their values of 1.77×10^{-4} for the dissociation constant, which is considerably different from values previously recorded by others, we have followed the method which Harned and Ehlers[3] employed for the determination of the ionization constants of acetic and propionic acids and have employed the cells

$$H_2 \mid HAc\ (m_1),\ KAc\ (m_2),\ KCl\ (m_3) \mid AgCl \mid Ag$$

In addition, we have obtained the experimental data which permits the computation of the ionization constant and heat of ionization from 0 to 60° at 5° intervals.

Experimental Results

The highest grade formic acid obtainable was twice fractionated by distillation. Carbonate-

(1) The material in this contribution is part of a Dissertation to be presented to the Graduate School of Yale University by Mr. Embree in partial fulfilment of the requirements of the degree of Doctor of Philosophy, June, 1934.

(2) Harned and Owen, THIS JOURNAL, **52**, 5079 (1930).

(3) Harned and Ehlers, *ibid.*, **54**, 1350 (1932); **55**, 652 (1933); **55**, 2379 (1933).