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-

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(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).

free potassium hydroxide solution was titrated against a hydrochloric acid solution the strength of which was obtained by gravimetric analysis. A formic acid solution of suitable strength was then analyzed by titration with the hydroxide solution.

The cell solutions were made first by adding appropriate amounts of acid and hydroxide solutions and then adding a weighed quantity of potassium chloride. The solution made in this manner was the most concentrated one of a given series. The cell solutions recorded in Table I were all made by dilution of this solution. Three series of measurements were made through the temperature ranges of 0 to 20°, 25 to 40°, 45 to 60°, respectively. The electromotive forces corrected to 1 atm. hydrogen pressure are given in Table I.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS H_2 | HAc (m_1), KAc (m_2), KCl (m_3) | AgCl | Ag

HAc = HCOOH

$m_1 = 0.8021\ m_2 = 0.9268\ m_3$	E_0	E_5	E_{10}	E_{15}	E_{20}
0.006451	0.56458	0.56748	0.57036	0.57323	0.57605
.01220	.54924	.55183	.55442	.55700	.55953
.02457	.53269	.53495	.53718	.53945	.54172
.03660	.52339	.52550	.52756	.52961	.53170
.04873	.51677	.51875	.52069	.52259	.52456
.09896	.50042	.50217	.50384	.50547	.50712
	E_{25}	E_{30}	E_{35}	E_{40}	
0.006538	0.57842	0.58115	0.58391	0.58764	
.01176	.56294	.56541	.56793	.57053	
.02445	.54398	.54612	.54835	.55054	
.03575	.53427	.53630	.53830	.54029	
.04863	.52647	.52839	.53024	.53208	
.09876	.50882	.51039	.51188	.51337	
	E_{45}	E_{50}	E_{55}	E_{60}	
0.006063	0.59160	0.59432	0.59704	0.59990	
.01238	.57152	.57391	.57635	.57889	
.02428	.55285	.55496	.55712	.55933	
.03645	.54165	.54369	.54570	.54770	
.04900	.53365	.53550	.53741	.53925	
.09895	.51468	.51625	.51788	.51947	

Calculations of the Ionization Constant and Heat of Ionization.—The equation for the electromotive force, E, of the cell may be transposed to

$$\frac{2.3026\ F}{RT}(E - E_0) + \log\frac{m_{\mathrm{HAc}}m_{\mathrm{Cl}}}{m_{\mathrm{Ac}}} = \log\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}\gamma_{\mathrm{HAc}}}{\gamma_{\mathrm{H}}\gamma_{\mathrm{Ac}}} - \log K = -\log K' \qquad (1)$$

E_0 is the normal potential of the cell, K is the ionization constant of formic acid, and the γ's and m's are the activity coefficients and molalities of the species denoted by subscripts. In order to compute K, we evaluated the left side of the equation which equals $-\log K'$ by employing the values of E_0 determined by Harned and Ehlers and then plotted this quantity against μ. As shown by Fig. 1, these plots were found to be straight lines and their slopes are given in the last column of Table II. The value of this function at zero μ is $-\log K$. One detail of this computation should be brought out at this juncture: m_{HAc} and m_{Ac}, the true molalities of undissociated formic acid molecule and formate ion must be evaluated by arithmetical approximation. As pointed out by Harned and Ehlers, this is necessary in the case of acetic acid and since the ionization constant of formic acid is ten times that of acetic acid, the second term on the left of the equation must be evaluated with some care. To effect this, a preliminary value of K was determined by substituting the stoichiometrical molalities, m_1, m_2 and m_3 for m_{HAc}, m_{Ac} and m_{Cl}, respectively, and extrapolating to zero μ. Since m_{HAc} equals $(m_1 - m_{\mathrm{H}})$, m_{Ac} equals $(m_2 + m_{\mathrm{H}})$ and m_3 equals m_{Cl}, it is only necessary to obtain m_{H}. This is accomplished by employing the thermodynamical equation for the ionization

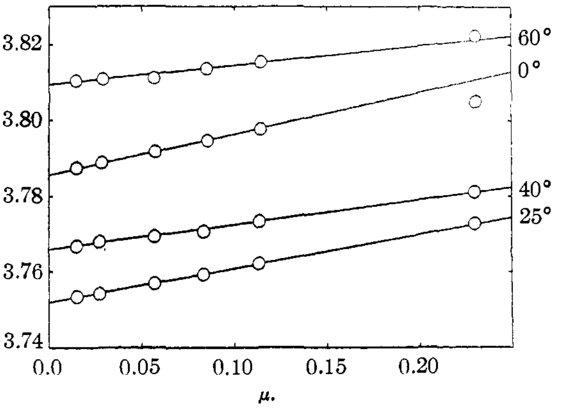

Fig. 1.—Graphs of $-\log K'$ against μ.

$$K = \frac{m_{\mathrm{H}}\ (m_2 + m_{\mathrm{H}})}{(m_1 - m_{\mathrm{H}})}\ \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{Ac}}}{\gamma_{\mathrm{HAc}}} \qquad (2)$$

It sufficed for our purpose to substitute for the activity coefficient product in this equation the values of $\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}$ in a potassium chloride solution which were determined by Harned and Hamer[4] through the required temperature range. Upon using the preliminary value of K, m_{H} was computed by equation (2). Corrected values of m_{HAc} and m_{Ac} were obtained, substituted in equation (1), and a second value of K determined.

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(4) Harned and Hamer, THIS JOURNAL, **55**, 2194 (1933).

This was used to redetermine m_H by equation (2), and the procedure repeated until the K and m_H values fulfilled the requirements of both equations. Three approximations were always sufficient.

The final values of K are given in Table II.

TABLE II

IONIZATION CONSTANT AND HEAT OF IONIZATION OF FORMIC ACID

t	$K \times 10^4$ (obs.)	$K \times 10^4$ Eq. 5	ΔH Eq. 6	ΔC_p Eq. 7	(Log K − Log K')/μ
0	1.638	1.642	931	−34.6	0.11
5	1.691	1.688	755	−35.9	.11
10	1.728	1.724	573	−37.1	.10
15	1.749	1.750	384	−38.4	.08
20	1.765	1.765	189	−39.7	.09
25	1.772	1.770	− 13	−41.0	.09
30	1.768	1.764	− 221	−42.3	.10
35	1.747	1.748	− 436	−43.6	.09
40	1.716	1.724	− 657	−44.8	.07
45	1.685	1.691	− 884	−46.1	.06
50	1.650	1.650	−1118	−47.4	.06
55	1.607	1.602	−1358	−48.7	.07
60	1.551	1.548	−1605	−50.0	.05

The heat of ionization was obtained by employing the equation

$$\Delta H = a + bT + cT^2 \qquad (3)$$

where a, b and c are constants and T is the absolute temperature. By substituting this function for ΔH in the van't Hoff equation and performing the required integration

$$\log K = -\frac{a}{2.303RT} + \frac{b}{R}\log T + \frac{c}{2.303R}T + I \qquad (4)$$

is obtained. Upon substitution of the observed values of K at the temperature in question, thirteen equations were obtained from which the values of a, b and c were computed by the method of least squares. The equation for log K with numerical coefficients was found to be

$$\log K = -(173.624/T) + 17.88348 \log T - 0.0280397\,T - 39.06123 \qquad (5)$$

and the equations for ΔH and ΔC_p were

$$\Delta H = 794.972 + 35.5613T - 0.12838T^2 \qquad (6)$$

and

$$\Delta C_p = 35.561 - 0.25679T^2 \qquad (7)$$

respectively. Values of these quantities computed from these equations are given in the third, fourth and fifth columns of Table II.

It is interesting to note that at 25° our value of 1.772×10^{-4} agrees closely with 1.77×10^{-4} obtained by Harned and Owen with the cells without liquid junction which did not contain the buffered solution. This agreement is within the estimated accuracy of both series of experimental results. As in the cases of acetic and propionic acids, K first increases, passes through a maximum at 25° and then decreases with increasing temperature.

Summary

1. From measurements of suitable cells, the ionization constant of formic acid has been determined from 0 to 60° at 5° intervals.

2. The ionization constant at any temperature from 0 to 60° may be computed by equation (5).

3. By equations (6) and (7) the heat of the ionization of the reaction, ΔH, and the difference in specific heats of the reactants and resultants of the ionization reaction may be computed.

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