effect indicates the velocity-determining reaction to be between two negative ions.

2. From the iodide catalysis can be calculated a constant for the bimolecular persulfate–iodide reaction; this constant is some 20–30% lower than when the velocity is measured independently, at least in solutions containing 0.02 *M* thiosulfate.

3. From the copper catalysis a constant can be calculated for the persulfate–copper ion reaction; the salt effect on this catalysis shows that the persulfate–copper ion reaction is between two negative ions, as might be expected from the fact that Cu^{++} is reduced and changed into a negative complex cuprous ion by thiosulfate.

4. The effect of sugar is to increase the velocity of the persulfate–thiosulfate reaction, and to increase the velocity of the persulfate–iodide reaction in the presence of thiosulfate in a somewhat abnormal fashion.

Further work on this reaction is in progress.

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A POTENTIOMETRIC STUDY OF ACID-BASE TITRATION SYSTEMS IN THE VERY STRONGLY ACID SOLVENT FORMIC ACID[1]

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If the ionization of an acid depends upon a reaction of the type

$$HCl + OH_2 \rightleftharpoons OH_3^+ + Cl^-$$

then the effect of the solvent upon the acidity of the solution obtained and upon the extent of the ionization may conveniently be separated into two factors.[2] One of these may be represented as the inherent basicity of the solvent and acts in such a way that a decreased basicity decreases the ionization of the acid but increases the acidity of the solution because the ionization takes place only as a result of the transfer of a proton from a weaker to a firmer binding. Thus hydrochloric acid is a strong electrolyte in water, but is only incompletely ionized in formic acid.[3] Nevertheless, indicator experiments show that the solution in formic acid is more acid than that in water. It is clear that the properties of a base should depend upon the acidity of the solvent in analogous fashion.

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[1] This article is based upon a dissertation submitted by Nicholas Dietz, Jr., to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1930.

[2] Hammett, THIS JOURNAL, **50**, 2666 (1928).

[3] (a) Schlesinger and Calvert, *ibid.*, **33**, 1924 (1911); (b) Schlesinger and Martin, *ibid.*, **36**, 1589 (1914).

The other factor is a medium effect which may be represented as the result of changes in ionic activity coefficients, that is, in the interionic electrical forces. A change in medium resulting in an increase in these forces results in a decreased ionization but probably in no great change in true acidity. Thus a solution of hydrogen chloride in ether is much less ionized than one in water. Basic indicators show decreased, acid indicators increased, acidity. It may further be expected that solvents of low dielectric constant, in which these forces seem always to be large, should exhibit large and specific salt effects. That is, relatively dilute electrolyte solutions in such a solvent should exhibit the same kind of complicated behavior as do very concentrated aqueous solutions. The potentiometric studies of Hall and Werner[4] on acetic acid solutions of bases seem to show this sort of effect in a pronounced degree.

It has seemed desirable to test further this point of view by the investigation of the properties as a solvent for acids and bases of a substance which is less basic and more acidic than water but which has the high dielectric constant and generally high solvent power for salts which may be taken to indicate interionic forces of relatively small magnitude.

We have therefore investigated potentiometrically solutions of acids and bases in formic acid. This solvent has a dielectric constant of 62.0 at 15°, it is a solvent for many salts,[5] including sodium and potassium chlorides; which have a very low solubility in most organic solvents, and solutions of salts give cryoscopic and conductivity values which correspond to extensive dissociation.[6] In these respects formic acid is much more like water than is such a solvent as acetic acid, in which salts give cryoscopic effects indicating association rather than dissociation[5] and conductivity dilution curves with maxima and minima. With respect to acidity and basicity, however, formic acid differs greatly from water, and solutions in it are even more deserving of the term superacid than are those acetic acid solutions in which Hall and Conant[7] did their pioneer work on the potentiometric investigation of strongly acid solvents. There is further interest in the potentiometric investigation of this solvent because of the existence of the precise and thorough conductivity studies of Schlesinger and his co-workers.[3,6]

In contrast the solvent offers considerable experimental difficulties. Solutions cannot be made anhydrous by the addition of an anhydride. The pure liquid decomposes slowly, and this decomposition is hastened by the presence of strong acids. We have found it impossible in spite of

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[4] Hall and Werner, THIS JORNAL, **50**, 2367 (1928).

[5] Zanninovich-Tessarin, *Z. physik. Chem.*, **19**, 251 (1898).

[6] References 3 and 5, also (a) Schlesinger and Coleman, THIS JOURNAL, **38**, 271 (1916); (b) Schlesinger and Mullinix, *ibid.*, **41**, 72 (1919); (c) Schlesinger and Reed, *ibid.*, **41**, 1921 (1919); (d) Schlesinger and Bunting, *ibid.*, **41**, 1934 (1919).

[7] Hall and Conant, *ibid.*, **49**, 3047 (1927).

very considerable investigation and the preparation of electrodes of a wide range of catalytic activity to obtain reliable hydrogen electrode potentials. Duplicate electrodes failed to agree and all electrodes adjusted themselves very slowly to changes in hydrogen-ion concentration. Nevertheless several titration curves were obtained with breaks qualitatively similar to those obtained with quinhydrone electrodes. Entirely satisfactory results were obtained with the *p*-benzoquinhydrone electrode. Even here, however, greater pains were necessary in the selection of electrodes than is the case in aqueous solutions, and it was necessary, moreover, to carry out measurements within a fairly short time interval because the potentials were found to drift in a negative direction (that is, in the direction of reduction) in acid solutions. Chloranil and 1,4-naphthoquinone were tried as substitutes for the benzoquinone, the former because it has no nuclear hydrogen and because it has been recommended by Conant and Hall for use in acetic acid solutions; the latter because it has a lower oxidation potential than benzoquinone. Chloranil seemed somewhat inferior to benzoquinone in definiteness and reproducibility. The behavior of the naphthoquinhydrone system is greatly affected by small variations in the method of preparation of the quinhydrone from the quinone. Some preparations gave results which were greatly superior to benzoquinone in reproducibility and freedom from drift in acid solutions, others were very inferior.

The method of investigation consisted in carrying out potentiometric titrations. Benzene sulfonic acid was found to be a suitable strong acid, as was expected from Hantzsch's indicator experiments. Sodium salts are in general strong electrolytes, and sodium formate if it is a strong electrolyte must have the greatest base strength possible in this solvent. As a reference half-cell we used a purely arbitrary constant system, and as a salt bridge a solution saturated with the very soluble sodium benzene sulfonate. There is of course no reason to believe that this bridge reduced the junction potential to zero, but it seems entirely probable that it should decrease to a small value the variation in contact potential with not too great changes in composition of the solution being titrated. The validity of the assumption seems justified by the results, as was the case with the similar scheme of Hall and Werner in acetic acid solutions.[4]

Materials

Formic Acid.—Kahlbaum 100% formic acid was first distilled in vacuo; the distillate was then purified by the method described by Coolidge.[8] The most highly purified acid had a melting point of 8.24°. The corresponding value obtained by Coolidge after more prolonged purification was 8.26°. The melting point was determined with the usual precautions, using a thermometer which was carefully compared with one recently calibrated by the Bureau of Standards. The purified acid was carefully pro-

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[8] Coolidge, This Journal, **50**, 2166 (1928).

tected from moisture and kept at a temperature of 10° to decrease the rate of decomposition. The purest acid (melting point 8.23 to 8.24°) was used for the titration cell solutions. Less highly refined acid (melting point 8.21 to 8.22°) was employed in the bridge and in the reference cell. Although formic acid is hygroscopic, it is not extraordinarily so: for example, a sample with a melting point of 8.05° was freely exposed to the atmosphere for thirteen minutes, after which the melting point had not changed measurably.

Sodium Formate.—The Kahlbaum salt was used after careful drying. Analysis by conversion to sodium sulfate gave a figure of 99.9%.

Benzene Sulfonic Acid.—After considerable difficulty with purchased material we made this substance by the method described by Fierz[9] for toluene sulfonic acid with excellent results. The aqueous solution after removal of sulfuric acid was evaporated to a sirup and then dehydrated and distilled at a pressure of 0.01 to 0.001 mm.[10] The white crystalline product was again distilled in a special apparatus, under the full vacuum of a diffusion pump with a liquid-air trap, and at a temperature of 120°, directly into glass bulbs, 10 to 15 mm. in diameter, which were then sealed off. By titration against sodium hydroxide free from carbon dioxide and standardized with Bureau of Standards benzoic acid it was found to have a purity of 99.7 to 99.9%. The anhydrous sulfonic acid is extremely hygroscopic. In preparation for a titration, a weighed bulb was broken in a dry mortar, and solution of the sulfonic acid in formic acid, which does not take place very rapidly, was allowed to proceed in the shelter of a desiccator kept dry with phosphorus pentoxide. After rinsing with formic acid, the glass fragments were collected and weighed.

Urea.—The sample melted at 133°.

Triphenyl Carbinol.—The Eastman Kodak product was used. It melted at 162.5°.

Benzoquinhydrone.—The Eastman Kodak product melting at 170–171° was used.

Apparatus and Method

The pyrex cell employed is illustrated in Fig. 1. It was found to be compact and convenient in use, and mixing of the solutions was avoided without the introduction of too great electrical resistance.

The electrodes were in most cases gold film burned on glass from a concentrated solution of pure gold chloride in glycerin containing a little oil of lavender. Electrical connection was established by a strip of platinum foil fused through the end of the glass tube which served as support. Before use they were cleaned with chromic acid, washed and heated to dull redness. Such electrodes gave very reproducible results, and readjusted themselves rapidly upon addition of acid or base. Electrodes of pure gold wire were found to give equally satisfactory results. Platinum electrodes were very unsatisfactory, showing differences of potential in a single solution of several millivolts. Gold plated platinum electrodes were no improvement upon bare platinum. This is in agreement with the observation frequently made in this Laboratory that platinum is particularly prone to contain electromotively active impurities. It is not clear, however, why these differences are so much greater in formic acid solutions than in aqueous ones. Two electrodes were always used in both titration and reference half-cells, and were frequently checked against each other during the course of the titration. The agreement obtained was approximately 0.1 millivolt.

In preparation for a titration, the salt bridge solution, consisting of formic acid saturated with sodium benzene sulfonate and carrying excess solid salt in suspension,

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[9] "Grundlegende Operationen der Farbenchemie," Zurich, **1920**, p. 190.

[10] The smaller apparatus described in the leaflet, "Synthetic Organic Chemicals," Vol. II, No. 3, issued by the Eastman Kodak Company, February, 1929, was used.

was introduced through a funnel into the salt bridge. The glass plugs were then firmly put into place with tongs, leaving a film of conducting solution around the sides of each plug. The excess solution squeezed out into the half-cells by this procedure was removed and the half-cells were rinsed several times with formic acid.

The solution to be titrated and the reference solution were then introduced into their respective half-cells. The reference solution consisted of formic acid saturated with sodium benzene sulfonate and containing 0.098 molar sodium formate. Quinhydrone was then added to both half-cells until an appreciable excess remained. Rough measurements indicated that the solubility of benzoquinhydrone in formic acid is about 0.1 molar.

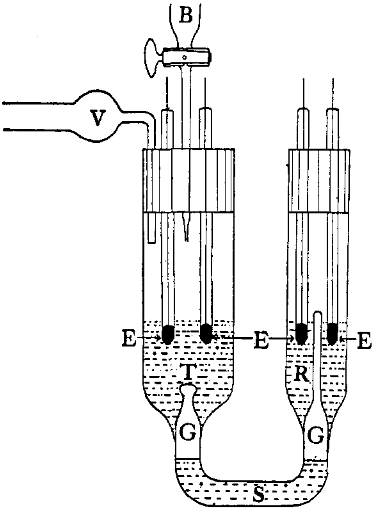

Fig. 1.—Titration cell. T, titration half-cell; R, reference half-cell; S, salt bridge; G, ground-glass plugs; E, electrodes; B, buret; V, vent.

Quinhydrone reacts slowly with formic acid in the presence of benzene sulfonic acid, the reaction being evidenced by a change in color with eventual formation of tarry products, and by a drift in potential toward less positive values. There was, however, no evidence of such reaction in sodium formate solutions, which are, of course, basic with respect to the solvent formic acid. For this reason titrations were started in basic solution, the reference half-cell solution was basic, and the titrations were completed within a time which experience showed would prevent a serious change in the potentials on the acid side of the end-point. The rate of potential drift was found to be 0.1 millivolt per minute in a 0.1 molar sulfonic acid solution, and not more than 0.01 millivolt per minute in a 0.025 molar sulfonic acid solution.

Before use all glassware was thoroughly baked at 110° and was stored over phosphorus pentoxide or otherwise protected from moisture. In use the vent of the cell and the opening of the buret were protected by tubes containing pentoxide.

All measurements were made at a temperature of 25.00°, maintained by immersion of the cell in a Freas water thermostat. A properly calibrated potentiometer and standard cell and a galvanometer with a sensitivity of 2602 megohms gave the electrical measurements a precision of one to two-tenths of a millivolt with the highest resistance cells used.

Sodium Formate Titrations.—In Tables I, II and III are listed the data for titrations by the above described method of various concentrations of sodium formate against benzene sulfonic acid. Under C_b are calculated the concentrations of sodium formate not neutralized, under C_a the concentrations of benzene sulfonic acid in excess of that required to neutralize the sodium formate. The calculations assume a simple and complete neutralization, volume additivity, and a specific volume of dissolved quinhydrone equal to that of the solid substance. The values in the column headed pK are calculated by the equation

$$pK = \frac{E_{ab}}{0.0591} - \log C_a C_b$$

TABLE I

TITRATION DATA

Sodium formate: benzene sulfonic acid (*p*-benzoquinhydrone electrodes). 0.001991 mole of sodium formate used (= 15.40 cc. of 0.1294 molar sodium formate); 0.4751 molar = titer of benzene sulfonic acid; 4.19 cc. of benzene sulfonic acid = theoretical end-point.

Acid added, cc.	X = fraction of base neut.	$E_{obs.}$, volt	E, volt, corr. to const. vol.	C_b	pK (ref. to C_a = 0.02482)
0	0	0.0252	0.0252	0.1294	5.425
0.31	0.074	.0262	.0267	.1174	5.451
1.13	.270	.0300	.0318	.0880	5.512
2.06	.492	.0367	.0399	.0580	5.579
2.96	.707	.0470	.0515	.03184	5.666
3.13	.747	.0498	.0546	.02718	5.688
3.31	.790	.0557	.0607	.02236	5.672
3.53	.843	.0627	.0681	.01657	5.684
3.67	.876	.0677	.0733	.01296	5.706
3.84	.917	.0781	.0839	.00865	5.705
3.98	.950	.0913	.0973	.00515	5.708
4.13	.986	.1162	.1224	.00146	5.833[a]
				C_a	pK (referred to C_b = 0.002718)
4.30	1.027	0.1450	0.1514	0.00265	5.753[a]
4.44	1.060	.1623	.1689	.00599	5.692
4.73	1.129	.1828	.1898	.01275	5.711
5.27	1.258	.1985	.2061	.02482	5.688
5.83	1.392	.2081	.2165	.0367	5.680
6.79	1.621	.2170	.2265	.0557	5.655
					Average 5.646

[a] Omitted in the average because of proximity to the end-point.

TABLE II

TITRATION DATA

0.001216 mole of sodium formate used (= 16.3 cc. of 0.07460 molar sodium formate); 0.4611 molar = titer of benzene sulfonic acid; 2.64 cc. = theoretical end-point.

Acid added, cc.	X = fraction of base neut.	$E_{obs.}$, volt	E, volt, corr. to const. vol.	C_b	pK (referred to C_a = 0.00860)
0	0	0.0374	0.0374	0.07460	5.657
0.45	0.171	.0403	.0410	.06021	5.701
1.64	.621	.0538	.0563	.02567	5.842
2.14	.811	.0713	.0745	.0125	5.858
2.62	.993	.126	.1299	.0005	6.34[a]
				C_a	pK (referred to C_b = 0.02567)
2.79	1.057	0.160	0.1641	0.00362	5.827[a]
3.00	1.136	.183	.1874	.00860	5.842
3.71	1.406	.2043	.2096	.02466	5.746
4.92	1.864	.2186	.2254	.04954	5.684
6.97	2.640	.2293	.2385	.08580	5.626
					Average 5.730

[a] Omitted in the average.

TABLE III

TITRATION DATA

0.0004367 mole sodium formate used (= 19.70 cc. of 0.02217 molar sodium formate); 0.4374 molar = titer of benzene sulfonic acid; 0.998 cc. = theoretical end-point.

Acid added, cc.	X = fraction of base neut.	$E_{obs.}$, volt	E, volt, corr. to const. vol.	C_b	pK (referred to C_a = 0.00489)
0	0	0.0706	0.0706	0.02217	5.788
0.309	0.310	.0761	.0765	.01507	5.862
.610	.611	.0912	.0920	.00836	5.862
.702	.703	.0980	.0990	.00635	5.867
.817	.819	.1096	.1107	.00386	5.886
.906	.908	.1238	.1250	.00195	5.942[a]
				C_a	pK (referred to C_b = 0.00836)
1.001	1.003	0.1417	0.1430	0.00042	5.304[a]
1.116	1.119	.1657	.1671	.00248	5.945
1.232	1.235	.1783	.1799	.00489	5.862
1.375	1.376	.1892	.1908	.00782	5.842
1.475	1.478	.1961	.1980	.00985	5.859
1.638	1.641	.2031	.2052	.01312	5.853
1.852	1.856	.2095	.2118	.01733	5.841
2.071	2.075	.2141	.2167	.02156	5.823
2.403	2.408	.2189	.2218	.02781	5.795
2.805	2.811	.2229	.2263	.03511	5.761
3.099	3.106	.2251	.2289	.0403	5.738
3.545	3.552	.2276	.2319	.0479	5.705
				Average	5.828

[a] Omitted in the average.

where E_{ab} is the observed difference in potential between a point on the acidic side and another point on the basic side of the titration end-point, all points on the basic side being referred to a single point (given in the heading of the column) on the acidic side, and all points on the acidic side being referred to a single point on the basic side. C_a is the concentration of sulfonic acid at the acid point and C_b the concentration of sodium formate at the basic point.

If the liquid junction potential remains constant during the titration, and if benzene sulfonic acid and sodium formate are completely ionized

$$E_{ab} = 0.0591 \log \frac{C_a f_a}{C_{ab} f_{ab}}$$

where C_{ab} is the concentration of hydrogen ion (probably $H_3CO_2^+$) in a solution of formate ion concentration C_b, f_{ab} is the activity coefficient of hydrogen ion in the same basic solution, and f_a is the activity coefficient of hydrogen ion in a solution of benzene sulfonic acid of concentration C_a. It follows that

$$pK = \frac{E_{ab}}{0.0591} - \log C_a C_b = -\log C_a C_b \frac{f_{ab}}{f_a}$$

With complete dissociation C_b is the concentration of formate ion in the basic solution, and C_{ab} is the hydrogen ion concentration of the same solution. The radio f_{ab}/f_a is nearly one, since it is the ratio of the activity coefficients of a given ion in two solutions of approximately the same total ion concentration. The quantity pK is therefore the negative logarithm of the product of the concentrations of the ions of the solvent, and the analog for formic acid of the quantity 14 for water.

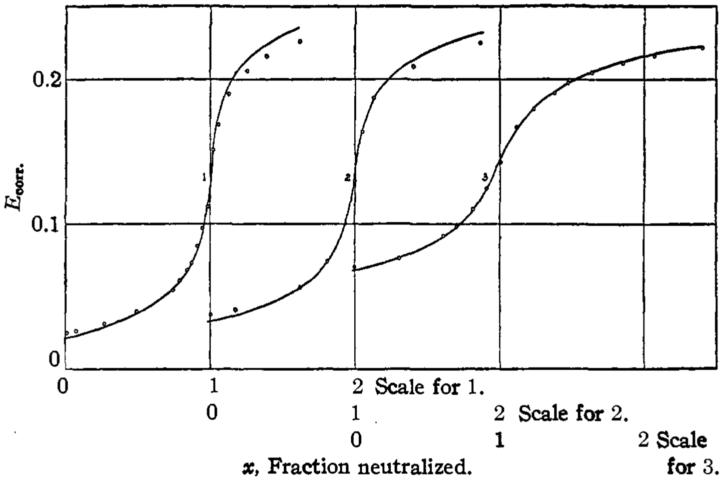

Fig. 2.

Figure 2 presents titration curves 1, 2 and 3 corresponding, respectively, to Tables I, II and III. The plotted points are the experimental values corrected to constant (initial) volume by means of the relationship

$$E_{corr.} = E_{obs.} + 0.0591 \log \frac{V_2}{V_1}$$

where V_2 is the volume corresponding to $E_{obs.}$ at any point during the titration and V_1 is the initial volume. The smooth curves are calculated by the equations

$$E = E_0 - 0.0591 \log [HCO_2']$$

$$X = 1 + \frac{K}{[HCO_2']C} - \frac{[HCO_2']}{C}$$

where X is fraction neutralized, C is the initial concentration of sodium formate, K is obtained from the average pK for the titration concerned, which is given in the tables, and E_0 is chosen by graphical methods to give the best fit. The latter of the above equations is essentially that of Eastman.[11]

Within a titration there is satisfactory agreement in the values of pK and likewise between observed and calculated curves. This would not be the

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[11] Eastman, This Journal, **47,** 332 (1925).

case if there were any great change in liquid junction potential during the titration; it would not be the case if either benzene sulfonic acid or sodium formate were anything but strong electrolytes in this medium; it would not be the case if the activity coefficients of hydrogen ion were subject to large specific effects instead of being determined principally by the total ion concentration. The *pK* values obtained do therefore give a real measure of the self-ionization of the solvent formic acid.

In the titration of certain apparently strong bases in the solvent acetic acid, Hall and Werner obtained curves which agree with the assumptions here used in the calculation of *pK*, but their titration curves for weak bases and their dilution curves for both strong and weak bases indicate the presence of very great salt effects accompanying the large changes in total ion concentration which occur in these cases but not in the titration of a strong base. Such intense interionic forces manifested by large salt effects are, however, absent in formic acid. Thus the *pK* is 5.65 at a salt concentration of 0.13 molar, 5.73 at a salt concentration of 0.075 molar and 5.83 at a salt concentration of 0.022. Furthermore, the agreement of these potentiometric values with the figure which may be calculated from the conductivity measurements of Schlesinger and his co-workers is as close as that of the corresponding values for aqueous solutions. They found at 25° a conductivity at infinite dilution for ammonium formate in formic acid of 70.4 r.o., for ammonium chloride of 52 r.o., and for hydrogen chloride of 75 r.o., the latter two values being somewhat uncertain on account of incomplete ionization of the hydrochloric acid and solvolysis of ammonium chloride. The conductivity 6.3×10^{-5} which was found for pure formic acid leads to a *pK* of 6.3, somewhat larger than our values, as it should be, since it is calculated for zero electrolyte concentration.

The titration data on the acid side of the end-point may be considered as a determination of the effect of varying acid concentration upon the hydrogen-ion activity with a constant concentration of salt present. This excess foreign electrolyte should tend to decrease variations in activity coefficients.[12] These dilution curves for benzene sulfonic acid in the presence of the three different salt concentrations are shown in Fig. 3, which also includes a dilution curve for benzene sulfonic acid without any salt present. The data for the last curve are given in Table IV. Where salt is present the curves are straight lines with the theoretical slope. In the absence of salt the slope is still about 70% of the theoretical value for a strong electrolyte.

From these various considerations it appears that formic acid is a solvent in which salt effects are not extraordinarily great as compared with water: in terms of a physical chemistry of solutions which has been based largely upon the study of aqueous solutions it may be called a normal solvent.

[12] Brönsted and Pedersen, *Z. physik. Chem.*, **103**, 307 (1922).

TABLE IV

DILUTION DATA: 0.4374 MOLAR BENZENE SULFONIC ACID IN THE ABSENCE OF SALT

Acid added to 10.18 cc. of formic acid, cc.	$E_{\text{obs.}}$, volt	Log C_a	Acid added to 10.18 cc. of formic acid, cc.	$E_{\text{obs.}}$, volt	Log C_a
0	0.1515	.....	0.75	0.2206	−1.523
0.07	.1794	−2.524	1.15	.2265	−1.354
.18	.1937	−2.119	1.81	.2318	−1.182
.28	.2033	−1.931	2.80	.2365	−1.027
.45	.2115	−1.733			

Because the ion product constant of formic acid is 10^8 times that of water, the break at the end-point of a titration is considerably less in formic acid than in water, and the range of acids and bases which can be titrated is more limited. A tenth normal solution of a base with an ionization constant less than 3×10^{-5} will give a titration curve with no inflection point.[13]

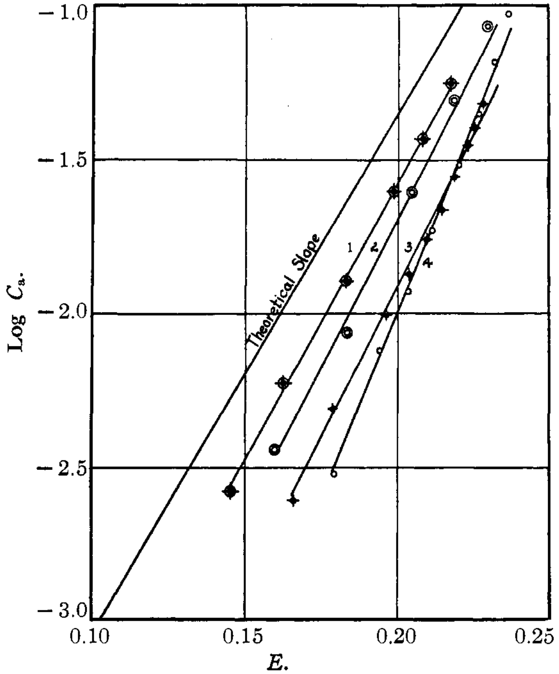

Fig. 3.—Dilution of benzene sulfonic acid Curve 1, data from Table I; Curve 2, data from Table II; Curve 3, data from Table III; Curve 4, data from Table IV.

If free hydrogen ions are incapable of existence in solution, and if ionization of a solvent depends upon its basicity as well as upon its acidity, the decrease in basicity in the transition from water to formic acid must be less than the increase in acidity.

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[13] Roller, THIS JOURNAL, **50**, 1 (1928).

Other Bases.—The behavior of several other basic substances in formic acid was investigated with the object of acquiring information as to the strengths of such substances in this solvent, and of learning more about the degree of acidity of the solvent itself.

To judge from color, benzene-azo-dimethylaniline and benzene-azo-diphenylamine are completely ionized, not only in formic acid but even in sodium formate–formic acid solutions. In water these indicators are so weakly ionized that their color changes occur at P_H 2.9–4.0 and P_H 1.2–2.1, respectively.[14]

Benzalacetophenone, which is so weak a base in acetic acid that it cannot be titrated,[15] imparts a yellow color to formic acid which is destroyed by the addition of a considerable quantity of sodium formate. This fading is due presumably to the reversal of the ionization

$$\underset{\text{colorless}}{B + HCO_2H} \rightleftharpoons \underset{\text{colored}}{BH^+ + HCO_2'}$$

Triphenylcarbinol is also so weakly basic in acetic acid that it cannot be titrated in that solvent.[7] It likewise gives a yellow solution in formic acid, which is decolorized by excess of sodium formate. Data for its titration with benzene sulfonic acid in formic acid solution are presented in Table V. The constancy of the *pK* values and their agreement with the values obtained with sodium formate show that it is a univalent strong electrolyte.

TABLE V

TRIPHENYLCARBINOL; BENZENE SULFONIC ACID (*p*-BENZOQUINHYDRONE ELECTRODES)

0.0002368 mole of triphenylcarbinol used (= 21.51 cc. of 0.01101 molar triphenylcarbinol); 0.4374 = titer of benzene sulfonic acid; 0.541 cc. of benzene sulfonic acid = theoretical end-point.

Acid added, cc.	x = Fraction of base neut.	$E_{obs.}$, volt.	E, volt (corr. to const. vol.)	C_b	pK (referred to C_a = 0.00583)
0	0	0.0951	0.0951	0.01101	5.88
0.112	0.207	.1000	.1002	.00869	5.90
.195	.360	.1053	.1055	.00698	5.91
.264	.487	.1132	.1135	.00557	5.87
.362	.668	.125	.1254	.00358	5.86
.481	.890	.1484	.1490	.00119	5.95[a]
				C_a	pK (referred to C_b = 0.00869)
0.631	1.165	0.1743	0.1750	0.00178	6.07[a]
.839	1.55	.1949	.1959	.00583	5.90
1.121	2.07	.2073	.2087	.01119	5.83
					Average 5.875

[a] Omitted in the average.

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[14] W. Mansfield Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Maryland, **1928**, p. 77.

[15] Conant and Hall, THIS JOURNAL, **49**, 3062 (1927).

There is evidence however that the ionization of triphenylcarbinol is more complex. Hantzsch[16] found that the freezing point depression which it produces in sulfuric acid indicates the formation of four instead of two products of ionization, probably by the reaction

$$(C_6H_5)_3COH + 2H_2SO_4 \rightleftharpoons (C_6H_5)_3C^+ + OH_3^+ + 2HSO_4^-$$

and Conant and Hall have found evidence that the reaction of the carbinol with strong acids in acetic acid solution produces water.

An ionization of the sort found by Hantzsch would make triphenylcarbinol act like a diacid base. That it acts here like a monoacid base corroborates the conclusion (for which direct evidence is given later) that water has a negligible basicity in formic acid. If the reaction is

$$(C_6H_5)_3COH + HCO_2H \rightleftharpoons (C_6H_5)_3C^+ + HCO_2^- + H_2O$$

the addition of water should decrease the formate-ion concentration and therefore increase the acidity. Using the utmost precautions to exclude water other than known amounts deliberately added, it was found that addition of water up to a concentration of 1% or 0.7 molar to a solution of triphenylcarbinol in formic acid was accompanied by a total increase in potential of only 0.0025 volt. This is an eighty-fold increase over the maximum concentration of water which, it is believed, could have existed in the original solution. The surprisingly small effect found may perhaps arise from a balancing of the above acidity-increasing reaction by a small basic ionization of the water, but some such reaction as

$$(C_6H_5)_3COH + HCO_2H \rightleftharpoons (C_6H_5)_3COH_2^+ + HCO_2^-$$

is also worthy of consideration. This is analogous to the reaction of hydroxo-pentammine cobaltic ion with acids.

Preliminary experiments with urea in formic acid indicated that a slow reaction involving changes in acidity takes place, and precise titrations were impossible. Nevertheless it was clear qualitatively that urea is a strong or moderately strong base in formic acid. Hall and Conant[7] found that urea is a very weak base in acetic acid, and its ionization constant in aqueous solution is only 10^{-14}.

The complete ionization of these bases, which are very weak in water and even in acetic acid, demonstrates the extremely high degree of acidity attainable in formic acid solutions.

If water and ether are bases in the sense that ammonia and the amines are, and there is much evidence to support such a conclusion, they are extremely weak bases, decidedly weaker than are urea and the halochromic ketones and carbinols. For example, 8.0 cc. of a 1.0 molar solution of water in formic acid titrated into 13 cc. of a 0.53 molar solution of benzene sulfonic acid caused a decrease in potential of only 0.025 volt. A large part of this change may be attributed to dilution of the acid alone. Like-

[16] Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907).

wise it was found that a 1.0 molar water solution was approximately 0.015 volt less acid than pure formic acid. Ether is also a very weak base: 7.4 cc. of a 1.0 molar solution of ether in formic acid added to 15 cc. of a 0.5 molar benzene sulfonic acid solution caused a potential change of only 0.026 volt, nearly half of which may be attributed to dilution.

The amounts of water and ether added in these experiments are so large and the changes in potential so small that a change in the nature of the solvent cannot be neglected as a possible source of part or all of the effect. The ionization constants (3×10^{-6} for water and 5×10^{-6} for ether) that may be calculated from these data cannot therefore be given much quantitative validity.

Measured by the ionization of dissolved weak bases, the solvent formic acid is very much more acid than the solvent acetic acid—the ratio of the acidity constants must be more than 10^4. Most of the difference is a medium effect rather than a difference in the inherent acidities of the two acids, for the ionization constant of formic acid in water is only ten times that of acetic acid in the same solvent. This difference in the properties as a medium is exactly what must be expected from the fact that formic acid is a better salt solvent, is a solvent in which interionic forces and therefore ionic activity coefficients are smaller than they are in acetic acid.[2]

Summary

1. Acid–base titrations have been carried out potentiometrically in the solvent formic acid. Benzene sulfonic acid has been found to be a strong acid, and sodium formate, triphenylcarbinol and urea have been found to be strong bases.

2. The ion product constant of the solvent has been calculated with a result in good agreement with that obtained from the conductivity data of Schlesinger. Its large value indicates that formic acid does not differ from water as much in basicity as it does in acidity.

3. Extremely pronounced salt effects were not found to occur in formic acid. In this respect it resembles water more than it does acetic acid.

4. Water and ether were found to have little or no basic properties in this solvent, and their basicities are therefore decidedly smaller than are those of urea and of the halochromic ketones and carbinols.

5. The ratio of the acidity of the solvent formic acid to that of the solvent acetic acid is much greater than the ratio of the acidities of the solutes formic and acetic acids in water. This is interpreted as the result of a medium effect predicted from other known properties of the two solvents.

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