PROPERTIES OF ACIDS AND BASES IN ACID SOLVENTS

V. POTENTIOMETRIC STUDY OF THE EFFECT OF ANHYDROUS FORMIC ACID ON THE STRENGTH OF ACIDS

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In the preceding papers it was shown that anhydrous formic acid has a high leveling effect on bases [1]. Both strong and extremely weak (in water) bases (pK about 13.8) acquire the same strength in formic acid. The number of substances developing basic properties in acid solvents in comparison with water has been considerably increased, this being bound up with the donor (protogenic) properties of acidic solvents.

Interest attaches to a study of the effect of acid solvents on the strength of acids. In this connection it is a general law that the number of substances possessing acidic properties in solvents with an acid character is considerably smaller than in water. The study of the individual properties of acidic solvents, however, has hitherto been neglected. Acidic solvents vary both in chemical and physical properties and these differences are bound to be reflected in the degree of their influence on the strength of acids.

In a series of papers it was established that acetic acid varies greatly in its effect. Organic acids which have high acidity in water (e.g. trichloracetic acid) become so weak in acetic acid that they do not titrate as acids [2] and exercise a negligible catalytic action [3]. This enabled us to effect fractional titration [2] of the mixture of acids:

$$HClO_4—H_2SO_4,\ HClO_4—HCl,\ CH_3C_6H_4SO_3H—HNO_3.$$

Formic acid differs markedly from acetic acid in the magnitude of its dielectric constant (57), which determines the electrostatic interaction of ions, as well as in the magnitude of the ionic product (pK_i of acetic acid is 12.6, that of formic acid is 6.3). It is therefore of interest to study the effect of formic acid on the strength of acids. In the first paper devoted to this problem, Zanninovich-Tessarin [4] arrived, on the basis of cryoscopic measurements, at the conclusion that the dissolved acids become associated in formic acid. The later investigations of Schlesinger [5] showed that anhydrous formic acid has a high dissociating action on salts and acids. An electroconductivity study of hydrochloric acid showed that the degree of dissociation of hydrogen chloride at a molar concentration of 0.0111 is 0.86, while at a concentration of 0.0518 M the value of α is 0.57.

Hammett and Deyrup [6] determined by an indicator method the strength (first constant) of sulfuric acid and benzene sulfonic acid. In this solvent they proved to be strong acids. The same authors obtained a value of $2 \cdot 10^{-6}$ for the second dissociation constant of sulfuric acid.

In the present investigation we attempted to obtain more systematic data for the effect of anhydrous formic acid on the strength of inorganic and organic acids, in view of the theoretical and practical importance of the problem.

EXPERIMENTAL

Anhydrous formic acid was prepared by the previously described method [1,5]. The following acids were studied:

$HClO_4$, HCl, H_2SO_4, $CH_3C_6H_4SO_3H$, CH_3COOH, CCl_3COOH, $CH_2ClCOOH$;

$(NO_2)_3C_6H_2OH$ and $C_6H_4OHCOOH$.

The first two of these were prepared by double decomposition in formic acid:

$$Ba(ClO_4)_4 + H_2SO_4 \rightarrow 2HClO_4 + BaSO_4,$$

$$BaCl_2 + H_2SO_4 \rightarrow 2HCl + BaSO_4.$$

The starting salts were pure grades, twice recrystallized from water and absolute alcohol. Barium salts were selected because $BaSO_4$ is the least soluble of all barium salts in formic acid. The sulfuric acid was twice distilled over bichromate. Admixture of 1.7 % water to the prepared acid led to a content of 0.02% water in the prepared 0.1 M solutions. Special experiments showed that such an admixture of water does not affect the potential of the quinhydrone electrode, as was also noted by Hammett and Dietz [7]. The precipitates of barium sulfate were not removed as a precaution against absorption of moisture by the solvent during the later operations. As was shown in later experiments, the precipitate had no appreciable effect on the results of titration. The amounts of salts and sulfuric acid were so selected as to give 0.1 M solutions of $HClO_4$ and HCl. In this connection it transpired that the double decomposition between $Ba(ClO_4)_2$ and H_2SO_4 in formic acid does not proceed to completion; instead of the anticipated 0.1 M solution of chloric acid, a mixture of chloric and sulfuric acids is obtained with a total concentration of 0.0885 M, while the proportion of chloric acid is 87%. Solutions of the remaining acids were prepared by dissolving definite weights of the pure anhydrous substances. The technique of investigation consisted in potentiometric titration of 0.1 M solutions of the acids with 0.2 M pyridine solution (pure, freshly distilled material) with a lamp potentiometer. The vessel used for the titration ensured exclusion of atmospheric moisture and was identical with that used in earlier work [1]. The electrochemical cell compound.

$$\text{Pt} \left| \begin{matrix}\text{acid} \\ \text{quinhydrone}\end{matrix} \right| \begin{matrix}\text{KCl} \\ \text{satd.}\end{matrix} \Bigg| \begin{matrix}\text{KCl} \\ \text{satd.}\end{matrix} \Big| Hg_2Cl_2 \Big| \text{Hg.}$$

in HCOOH in H_2O

Titration was performed with quinhydrone and glass electrodes. This was done not only because it was of interest to compare the obtained results and to secure supplementary evidence for the possibility of utilizing the glass electrode in nonaqueous (acidic) media, but also because hydrogen chloride in anhydrous formic acid reacts with quinhydrone and the mixture titrates like the pure solvent. The possibility of utilizing the quinhydrone electrode in formic acid solutions has already been demonstrated [1, 7]. In our work the glass electrode has been repeatedly used for titration in acetic acid. Its potential was rapidly established and remained stable. The possibility of using it in acetic acid solution was demonstrated by the special investigations of Izmailov and Aleksandrova [8]. Attention should be drawn to one special feature of the glass electrode in acid solvents: The potential of the glass electrode during potentiometric titration remains stable for some time (10-15 titration curves), but subsequently the electrode potential is not stable. If the inner solution (Weibel solution) at the electrode is replaced by fresh solution, then the electrode functions again, and the potential is again stabilized but at a value considerably lower than the original potential in otherwise identical conditions.

The plots of titration of the acids at the quinhydrone and glass electrodes exhibit differences in the alkaline region (Fig.1). (We consider solutions containing an excess of $HCOO^-$ ions to be alkaline). The potential jump at the equivalent point is considerably lower for curves plotted with the glass electrode. However, the ratio of the dissociation constants of acids, calculated from the titration curves, was identical for both electrodes. We were thus able, on the basis of glass electrode data, to calculate the dissociation constant of HCl.

Consequently the glass electrode gives a serious error in formic acid in the alkaline region, and this limits its application in formic acid solutions.

Data have been published [5] for 0.1 M solutions of hydrogen chloride in anhydrous formic acid, but we failed to obtain reproducible results for these solutions; titration values varied the whole time even with a reduced amount of HCl, and only after keeping the solution for seven days were reproducible results obtained when titrating half the amount of introduced acid. Since pyridine and HCl form the compounds $Py \cdot 2HCl$ and $Py \cdot HCl$, the half amount may be due to the formation of $Py \cdot 2HCl$. This possibility was not confirmed, however, in titration with sodium formate, and we reached the conclusion that the variable results were due to volatilization of HCl. In the later experiments on HCl titration, therefore, we used 0.05 M solution. The potential of the glass electrode was then satisfactorily reproduced and the equivalence point on the curve was close to the theoretical value. The remaining acids did not introduce any complications.

In Fig. 2 are plotted the titration curves. Their character is that usual for acid-base titrations.

As in the previous cases the effect of formic acid on the strength of the acids was quantitatively evaluated by calculating the dissociation constants with the help of the Roller equation [9].

$$\epsilon = 200\sqrt{K}\sinh\Delta,$$

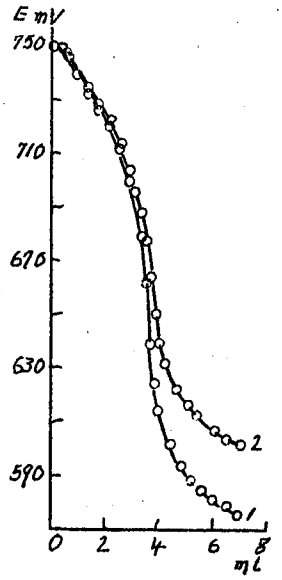

Fig. 1. Titration curves of toluenesulfonic acid in anhydrous formic acid. 1) With quinhydrone electrode; 2) with glass electrode.

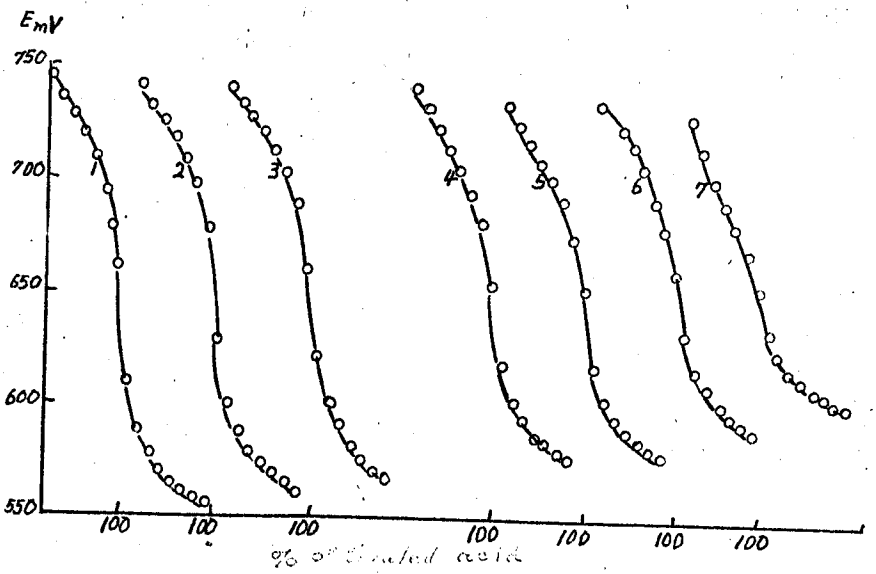

Fig.2. Titration curves of acids in anhydrous formic acid. 1) Chloric; 2) toluenesulfonic; 3) sulfuric with quinhydrone electrode; 4) chloric; 5) toluenesulfonic; 6) sulfuric; 7) hydrochloric, with glass electrode.

where ϵ is the percentage titer error;
Δ is the potential jump in millivolts corresponding to the given titer error multiplied by 0.158;
K is $K_i/C_A K_A$, where K_i is the ionic product of the solvent; K_A is the sought for dissociation constant of the acid; C_A is the salt concentration at the stoichiometric point.

pK_i was calculated from the titration data in accordance with the procedure of Hammett and Dietz [7]. The value of pK_i was corrected for the salt error by the formula

$$pK_i = pK_i' + 2A\sqrt{\mu},$$

where pK_i' is calculated from the titration data;

$A = 0.5(D_{H_2O}/D_{HCOOH})^{3/2}$; D is the dielectric constant; μ is the ionic strength.

No correction is introduced for the error in the degree of dissociation, since the investigated acids and the base used for titration are substantially completely dissociated in formic acid. The resultant value of the ionic product of the solvent in presence of chloric acid (the strongest acid) was equal to 5.77 in the case of the quinhydrone electrode. This value was also taken for calculation of the dissociation constants of acids in the Roller formula cited above.

The obtained pK values for the acids are listed in the table side by side with the pK values of the same acids in acetic acid, calculated by Izmailov [10].

It was found that acetic acid, the chloroacetic acids, salicylic acid and picric acid are so weakened both in formic and acetic acid that they do not titrate as acids. This property may be exploited for fractional titration of mixtures of inorganic and organic acids in formic acid as solvent. Thus the utilization of this solvent both for determination of bases [1] and for fractional titration of acid mixtures widens the potential scope of acid-base titration.

The dissociation constant of HCl in formic acid was calculated from the conductometric data of

TABLE

Dissociation Constants of Acids in Anhydrous Formic Acid and Acetic Acid

Acid	pK_{HCOOH}		pK_{CH_3COOH}
	quinhydrone electrode	glass electrode	
Chloric	0.28	0.56	5.80
Toluenesulfonic	0.34	0.73	—
Sulfuric	0.58	0.94	8.20
Hydrochloric	0.89*	1.23	8.85
Trichloroacetic	—	—	11.46

* pK was calculated from the mean shift of pK of the acids as calculated from the glass and gum hydrone electrode titration curves.

Schlesinger and Martin [5]. The value of the constant for a concentration of 0.0518 M was 0.0385, equivalent to pK = 1.41. Our calculations give a value of pK = 1.23 for 0.05 M HCl. The good agreement for HCl indicates the accuracy of our pK values for the other acids.

Hammett and Deyrup [6] determined the second constant of H_2SO_4 by an indicator method. Since the value of $2 \cdot 10^{-5}$ for the second constant is very close to the value of the ionic product of the solvent, sulfuric acid in formic acid may only be titrated as a monobasic acid. Titration of sulfuric acid in acetic acid, whose ionic product is $2.5 \cdot 10^{-13}$, shows that H_2SO_4 behaves like a monobasic acid in this solvent, probably for the same reason (the value of the second constant of H_2SO_4 is close to the ionic product of acetic acid.

We know that Hantzsch correlated the effect of a solvent on the properties of acids mainly with the chemical transformations of acids under the influence of the solvent due to reaction of acid with solvent. Hantzsch relegated the physical properties of the solvent to a secondary place. Comparison, however, of the obtained data for acid strengths in acidic solvents (formic and acetic acids) is indicative of the very important role of the dielectric constant of the solvent. Inorganic acids in formic acid (DC = 57) are considerably weaker than in acetic acid (DC = 6). Whereas acetic acid alters the strength of inorganic acids to such a degree that some of them can be fractionally titrated, the inorganic acids which are strong in water remain strong in formic acid, although they become somewhat weaker than in water.

SUMMARY

1. A study was made by the method of potentiometric titration of the effect of anhydrous formic acid on the strength of inorganic and organic acids (chloric, sulfuric, hydrochloric, toluenesulfonic, trichloroacetic, monochloroacetic, picric, acetic and salicylic).

2. It was shown that inorganic acids remain strong in anhydrous formic acid; formic acid differs from acetic acid in not possessing a modifying effect on the strength of inorganic acids, due to the high dielectric constant of formic acid. Organic acids become so weak in formic acid that they do not titrate like acids. This characteristic may be utilized for fractional titration of mixtures of inorganic and organic acids.

3. The dissociation constants of chloric, sulfuric, hydrochloric and toluenesulfonic acids were calculated from the titration data.

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