QUALITATIVE TESTS IN FORMIC ACID MEDIUM

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HARDT and ECKLE [1] were the first to investigate systematically the possibilities of qualitative tests and separations in glacial acetic acid. Besides finding some new prospects of the method they have found disadvantageous that inorganic salts were not readily dissolved in the medium. On this basis the investigation of the qualitative reactions and separation methods, applied up to then with water, seemed to be interesting using some other non-aqueous solvent. Mainly solvents similar to water were chosen which contained proton and were apt to autoprotolysis, and by which inorganic salts were expected to be dissolved, dissociated and solvated.

In the present paper the investigation of the reactions of cations in formic acid will be reported. In this case, besides the mentioned solvent properties also special and favourable behaviour were expected owing to the strong reducing power of formic acid. Absolute formic acid, owing to its unstability and hygroscopic nature was found to be less suited to practical purposes than formic acid obtained from analytical grade formic acid containing little water (less than 3%) by distillation and did not offer analytical advantages over the latter in the great number of cases studied. So the solvent obtained from commercial analytical grade formic acid by distillation was used without absolutization. The water content was found to increase by maximum 0.1% per month when stored in a glass-stoppered vessel in refrigerator, therefore no further precaution was necessary.

In the course of the experiments the perchlorates of cations were used, these having a high degree of dissociation, and being readily dissolved by formic acid. The 0.1 M solutions of metal perchlorates in formic acid were prepared and used in the experiments. The solutions of bismuth and tin perchlorates in formic acid were acidified with perchloric acid. Reagents were also prepared with formic acid as solvent, their concentration being 0.1 M, e.g. ammonium bromide, ammonium iodide, sodium formate etc.

Formic acid solutions of hydrogen sulphide and hydrogen chloride gases saturated at atmospheric pressure with concentrations 8,67 g H_2S/l and 81.1 g HCl/l were also prepared.

The qualitative analytical reactions investigated are described below. The composition of precipitates obtained in formic acid was checked by analytical methods.

Reactions of silver(I) ions

Silver ions yield black silver sulphide precipitate with sulphide, white silver chloride precipitate with chloride, pale yellow silver bromide precipitate with bromide, pale yellow silver iodide with iodide ions. On adding sodium formate to the formic acid solution of silver(I) ions a black precipitate was formed slowly, which was found to be metallic silver.

Reactions of lead(II) and mercury(II) ions

(The solution of mercury(II)perchlorate in formic acid was always freshly prepared, since the salt was reduced by the solvent on storing.) In formic acid lead(II) and mercury(II) ions react with sulphide, chloride, bromide and iodide ions similarly as in water. No precipitate is formed when sodium formate is added to their 0.1 M solutions, but white lead(II)formate and mercury(II)formate precipitates appear on adding the reagent to more concentrated solutions.

Reactions of copper(II)ions

Brownish black copper(II)sulphide precipitated when sulphide ions were added to the solution of copper(II)ions in formic acid. On adding chloride ions to the blue solution of copper(II) perchlorate in formic acid the solution turns green, the reddish brown copper(II)chloride fields slowly a precipitate soluble in water. Copper(II)ions form black copper(II)bromide precipitate with bromide ions in formic acid, which is dissolved in excess reagent as a wine-red complex. Copper(II)bromide is also soluble in water. On adding iodide ions to the solution of copper(II)ions, white copper(I) iodide precipitate and iodine are formed. When sodium formate is added to the formic acid solution of copper(II)perchlorate, the solution turns dark blue, but no precipitate is formed.

Reactions of cadmium(II) ions

In the solution of cadmium perchlorate in formic acid yellow cadmium sulphide precipitate is formed with sulphide ions. On adding chloride, bromide or iodide ions, white cadmium chloride, cadmium bromide and cadmium iodide precipitates are formed, respectively, which are dissolved by excess reagent while the corresponding halide complexes are formed. On passing hydrogen sulphide gas through the solutions of the halide complexes, no cadmium sulphide is precipitated. The complexes can be decomposed by water. From a fairly concentrated solution of cadmium perchlorate in formic acid, white cadmium formate is precipitated by formate ions.

Reactions of bismuth(III) ions

A black bismuth(III)sulphide precipitate is formed by sulphide ions in the formic acid solution of bismuth perchlorate. On adding chloride or bromide ions to the formic acid solution of bismuth(III)ions, colourless halogen complexes are formed. When hydrogen sulphide gas is passed through the solution of the halogen complexes, no bismuth sulphide precipitate is formed. Water reduces the stability of the complexes. On adding iodide ions to the formic acid solution of bismuth ions a black bismuth(III)iodide precipitate is formed, which gives a colourless solution on adding excess reagent. Formate ions give white bismuth(III)formate with bismuth(III)ions.

Reactions of arsenic(III)ions

All reactions were carried out with sodium arsenite in formic acid. From the acidifies solution of arsenic(III) ions in formic acid arsenic(III)-sulphide is formed quickly and quantitatively on introducing gaseous hydrogen sulphide. The precipitate is not dissolved by a 2M solution of sodium formate or ammonium formate in formic acid. No change can be observed on the addition of chloride or bromide ions to the original solution. With iodide ions yellow arsenic(III)iodide precipitate is formed which is dissolved in water by hydrolysis.

Reactions of antimony(III)ions

Sulphide ions form an orange antimony(III) sulphide precipitate with antimony(III) which is not dissolved in the 2M solution of sodium formate or ammonium formate in formic acid which latter also contains hydrogen sulphide. On adding chloride and bromide ions to the solution of antimony(III) ions no change can be observed. Iodide ions form orange antimony(III)iodide precipitate which is dissolved in excess reagent. On adding formate ions to the solution of antimony(III)ions in formic acid a white antimony(III)formate precipitate is formed, which is dissolved by excess reagent.

Reaction of tin(II)ions

Sulphide ions form brown tin(II)sulphide precipitate with tin(II)ions in formic acid. The precipitate is not soluble in a 2M solution of sodium formate or ammonium formate which also contains hydrogen sulphide. On adding chloride or bromide ions to the solution of tin(II)perchlorate, white tin(II)chloride or tin(II)bromide precipitate is formed. Both precipitates are soluble in excess reagent. Tin(II)ions form a yellow tin(II)iodide precipitate with iodide ions in formic acid. The precipitate is not dissolved in excess reagent. Sodium formate forms white tin(II)formate precipitate with tin(II)ions in formic acid, which is dissolved by excess reagent.

Reactions of zinc(II)ions

On adding sulphide ions to the solution of zinc(II)perchlorate in formic acid a white zinc(II)sulphide is formed. No precipitate appears when chloride, bromide or iodide ions are added to the solution of zinc(II)ions in formic acid, but no zinc sulphide is precipitated on passing hydrogen sulphide through the solution of zinc ions in formic acid which also contains halide ions. The stability of zinc halide complexes is reduced by water, as indicated by the fact that zinc sulphide precipitates from the solution of zinc halide complexes in the presence of sulphide ions when water is added. Formate ions form white zinc formate with zinc ions, which is dissolved in excess reagent.

Reactions of cobalt(II)ions

No cobalt(II)sulphide is precipitated from the solution of cobalt(II)ions in formic acid on introducing gaseous hydrogen sulphide. On adding a 2M solution of sodium formate in formic acid containing also hydrogen sulphide to the solution of cobalt(II)perchlorate a pink cobalt(II)formate precipitate is formed which is not soluble in excess reagent.

On adding chloride, bromide or iodide ions to the pink solution of cobalt(II)perchlorate in formic acid it turns blue, greenish blue and green, respectively. On adding water to any of the three solutions, the original colour restores.

Reactions of nickel(II)ions

No nickel(II)sulphide is precipitated when gaseous hydrogen sulphide is passed through the solution of nickel(II)ions in formic acid. When a 2M solution of ammonium formate in formic acid which also contains hydrogen sulphide is added to the solution of nickel(II)perchlorate, a green nickel(II) formate precipitates. The precipitate is insoluble in excess reagent. On adding chloride, bromide or iodide ions to the green solution of nickel perchlorate it turns pale green, yellowish green and yellow, respectively. The original colour can be restored in all three cases by adding water.

Reactions of iron(II)ions

Iron(II)sulphide is not precipitated from the solution of iron(II)ions in formic acid when gaseous hydrogen sulphide is passed through it, or when a 2M solution of ammonium formate in formic acid also containing hydrogen sulphide is added to it. In the second case an off-white iron(II) formate precipitate is formed. On adding chloride or bromide ions to the yellowish brown solution of iron(II) perchlorate in formic acid it turns to green and dark brown, respectively. The colour restores in both cases on adding water. With iodide ions black iron(II)iodide is precipitated which is partly dissolved in excess reagent with wine-red colour.

Reactions of aluminium(III)ions

No aluminium sulphide is precipitated from the formic acid solution of aluminium perchlorate when hydrogen sulphide is passed through it or a 2M solution of ammonium formate in formic acid which also contains hydrogen sulphide is added. In the second case a white aluminium formate precipitate is formed slowly, which is insoluble in excess reagent. No change can be observed when chloride, bromide or iodide ions are added to the formic acid solution of aluminium perchlorate.

Reactions of chromium(III)ions

No precipitate is formed when hydrogen sulphide is passed through the solution of chromium(III)ions in formic acid or a 2M solution of ammonium formate also containing hydrogen sulphide is added. On adding chloride, bromide or iodide ions to the blue solution of chromium(III)perchlorate in formic acid it turns apple-green, green and yellowish green, respectively.

Reactions of manganese(II)ions

Manganese(II)sulphide is not precipitated when hydrogen sulphide is passed through the solution of manganese(II)perchlorate in formic acid, or a 2M solution of ammonium formate in formic acid containing also hydrogen sulphide is added. In the second case, however, white manganese(II) formate precipitate is formed. No change occurs when chloride, bromide or iodide ions are added to the solution of manganese(II) ions in formic acid.

Reactions of calcium(II), strontium(II) and barium(II)ions

White calcium sulpfate, strontium sulphate and barium sulphate are precipitated by sulphate ions from the formic acid solution of calcium, strontium and barium ions, respectively.

Neither of the three ions form precipitate with carbonate and halide ions in formic acid solution.

As reflected by the experiments described above, the behaviour of most ions is different in formic acid from that in water. The most striking difference is that cations cannot be classified on the basis of the solubilities of their sulphides and carbonates in formic acid. It has been expected that the carbonates are dissolved in formic acid in a solvolytic reaction, so they cannot be used for the separation of class 4 cations, but the extraordinary behaviour of metal sulphides was surprising.

In water, class 2 cations form precipitate with hydrogen sulphide, which, owing to the amphoteric nature of these cations, behave as thioacids and are dissolved in the thiobase $(NH_4)_2S$ to form thiosalts. The dissolution can be described by the following reaction equation:

$$X_2S_3 + 3\,S^{2-} \rightleftharpoons 2XS_3^{3-}$$

where X is antimony(III) or arsenic(III). The dissolution, as reflected by the reaction equation, is closely related to the concentration of sulphide ions in the solution. In a 2M aqueous solution of $(NH_4)_2S$ the concentration of sulphide ions is about 10^{-3} g ion/l. The sulphides of class 2 cations can only be dissolved in a reagent with a sulphide ion concentration of at least 10^{-3} g ion/l, or higher. The reagent which corresponds to aqueous ammonium sulphide in formic acid is the solution of ammonium sulphide in formic acid is the solution of ammonium formate in formic acid which also contains hydrogen sulphide. According to the experience of the authors, the sulphides of class 2 cations cannot be dissolved by this reagent. The reason for this is the low sulphide ion concentration in formic acid. Hydrogen sulphide is a weak acid even in water, which dissociates in two stages. The dissociation constant $K_D \approx 10^{-22}$. Owing to the acid character of the solvent the dissociation of hydrogen sulphide is suppressed in formic acid, hence, the sulphide ion concentration is lower. Solvents can change the strengths of dissolved acid-base pairs by solvolytic and dielectric effects.

The solvolytic effect of solvents depends on the proton affinity thereof. Since formic acid is less basic than water, it suppresses the dissociation of hydrogen sulphide.

The dielectric constants of solvents influence the strengths of the acid-base pairs, for which there occurs an electrostatic attraction between the new acid and base formed during solvolysis.

According to GILKERSON [2] the following relationship exists between the negative logarithm of the dissociation constant, P_{KD}, and dielectric constant of the medium:

$$p_{KD} = p_{K_0} + \frac{A}{\varepsilon}$$

where p_{K_0} and A are constants for a given solvent and acid-base pair, pK_0 is characteristic of the dipole moment of the solvent and acid-base pair, while A of the charge and radius of particles.

The dissociation of hydrogen sulphide is smaller in formic acid than in water owing to the lower dielectric constant of the former.

The difference p_{Ks} of the p_{KD} values of an acid-base pair in water and in the solvent S, is characteristic of the p_{KD} value of any acid-base pair of the same type. According to CHARLOT [3], for acid-base pairs of the type HA/A^- the p_{Ks} value for water and formic acid is —4.5 pH unit. The variation of the dissociation constant of hydrogen sulphide on introducing it into formic acid instead of water can be given as follows:

$$(p_{KD})_{H_2O} - (p_{KD})_{HCOOH} = -4{,}5\,.$$

The dissociation constant of hydrogen sulphide in water $K_D \approx 10^{-22}$. From this

$$22+4{,}5 = (p_{KD})_{HCOOH}\,,$$

whence the dissociation constant of hydrogen sulphide in formic acid $K_D = 3 \cdot 10^{-27}$. The concentration of sulphide ions can be calculated as follows:

$$\frac{[H^+]^2\,[S^{2-}]}{[H_2S]} = 3 \cdot 10^{-27}\,.$$

The concentration of saturated hydrogen sulphide in formic acid is $0.2 \cdot 10^{-1}$ M, i.e.

$$[S^{2-}] = \frac{6 \cdot 10^{-28}}{[H^+]^2}\,.$$

Applying the values of the pH as defined for water:

at pH = 0 $\quad [S^{2-}] = 6 \cdot 10^{-28}$
at pH = 3 $\quad [S^{2-}] = 6 \cdot 10^{-22}$
at pH = 6 $\quad [S^{2-}] = 6 \cdot 10^{-16}$

The sulphide ion concentration is about 10^{-13} times smaller in a 1M solution of ammonium formate in formic acid containing hydrogen sulphide than in the 1M solution of ammonium hydroxide in water containing hydrogen sulphide, which is not enough for the thio-acids to be dissolved.

Also the fact that the sulphides of group 3 metal ions cannot be precipitated in formic acid, except for zinc, is due to the reduction of sulphide ion concentration.

If a metal sulphide, MeS is precipitated quantitatively, its concentration in the solution will fall below 10^{-5} g ion/l.

Inserting into the solubility product this value and the sulphide ion concentration of a 1M ammonium formate solution in formic acid containing hydrogen sulphide we get:

$$L = [10^{-5}],\ [10^{-16}] = 10^{-21}$$

which means that only sulphides with a solubility exponent pL greater than 21 can be precipitated in formic acid.

In Table 1 some literary data [4, 5, 6] for the solubility exponents of metal sulphides of the type MeS in water are listed. As a first approximation, it was assumed that the solubilities in formic acid are equal to those in water. The sulphides which are precipitated in formic acid can be predicted from the data in Table 1. Although the calculations used involve some neglection, the data in the table agree well with experience.

Table 1

The solubility exponent of the metal sulphides

MeS	pL
PtS	70
HgS	52.4
CuS	44.07
PbS	29
SnS	28.1
CdS	28.4
ZnS	22.9—25.2
α-CoS	22.2
α-NiS	21
FeS	19
MnS	15

Zinc sulphide can be precipitated in formic acid while cobalt(II), nickel(II), manganese(II) and iron(II) sulphides cannot.

It was found that silver formate decomposed in formic acid to form metallic silver, owing to the reducing power of the solvent. On the other hand, the solution of silver perchlorate in formic acid is stable for some days. On adding a formic acid solution of sodium formate to the solution of silver perchlorate in formic acid, metallic silver precipitates. This can be attributed to the fact that the $[H^{+}_{\text{solv.}}]$ concentration is reduced by formate ions, the reducing power of the system increases and formic acid will reduce silver ions.

According to the experience of the authors, besides Ag(I)ions also Hg(II) ions are reduced by formic acid. Salts which contain nitrate, chromate peroxidisulphate, chlorate or permanganate ions and are soluble in formic acid, react with the solvent.

Some difference was found in the behavioür of metal halides in formic acid as compared to water. Cu(II)Cl_2, Cu(II)Br_2, $CdCl_2$, $CdBr_2$, Sn(II)Cl_2, Sn(II)Br_2, Sn(II)I_2, As(III)I_3 and Fe(II)I_2 are less soluble in formic acid than in water.

Part of the salts mentioned are weak electrolytes even in water. Their solubility is lower in formic acid owing to the smaller dielectric and solvolytic effect of the solvent. Great part of metal halide precipitates is dissolved by excess reagent while soluble complexes are formed. The increased stability of the complexes is also due to the nature of the solvent.

Summary

Some analytical reactions were studied in formic acid medium. Owing to the solvolytic, dielectric and reducing effect of the solvent several reactions were found to proceed differently in formic acid than in water. In formic acid the separation system based on the different solubilites of sulphides and carbonates is not suitable for the classification of cations. The sulphides of class 2 cations are not dissolved by the solution of ammonium formate in formic acid containing hydrogen sulphide, and the reagent does not precipitate the sulphides of class 3 cations except for zinc, the sulphide of which is precipitated even by hydrogen sulphide. The carbonates of class 4 cations are soluble in formic acid. So the cations studied can be separated into two groups according to whether they form precipitate with hydrogen sulphide or not.

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