[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Acid Strength of Inorganic Cations and the Basic Strength of Inorganic Acetates in Acetic Acid.[1] II

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According to Brönsted's terminology solvated cations may be considered as acids. The acid character of various cations in aqueous medium is determined by the tendency of the hydrated ions to split off protons. The acid reaction of the hexaquoaluminum ion for example may be represented by the reaction

$$Al^{+++}(H_2O)_6 \rightleftharpoons Al^{+++}(H_2O)_5OH^- + H^+$$

The acidity of inorganic cations increases with decreasing size and increasing charge of the ion. With the alkali ions it is hardly possible to show the relation between size and acidity since salts of the strong acids of the most extreme members of the group, cesium and lithium, hardly change the reaction of water. Differences in acidic and basic properties are much more pronounced in glacial acetic acid than in water; for this reason a study was made to establish the above relationship. In the first place, the electrical conductivities of 0.02 molar solutions of various acetates in acetic acid were measured at 25°. Assuming that the polyvalent acetates dissociate in the same way as the monovalent acetates, and that the mobilities of the various cations are the same (which is not correct), the specific conductances measured give the order of the basic strengths of the various bases. The results were verified by an entirely different method. To the 0.02 molar solution of the acetate a suitable indicator, assuming an intermediate color in the solution, was added and the concentration of potassium acetate sought which imparted the same color to the indicator. Thus, all readings are related to potassium acetate as standard, although it should be mentioned that the latter is not completely dissociated in acetic acid even at high dilutions. Various organic bases are more strongly dissociated than potassium acetate at the same concentration. The methods used yielded the same order of basicity for the various acetates, and the agreement from the quantitative viewpoint was very gratifying. In order to correlate our results with those of N. F. Hall[2] some organic bases were investigated in a way similar to that used for the inorganic acetates.

Materials.—The same substances were used as described in a previous paper.[3] In addition the following substances were prepared.

Aniline.—A c. p. product, distilled from zinc dust and twice redistilled. The fraction boiling between 180.0 and 180.6° at 74 mm. was collected.

Strontium, Manganese, Lithium, Nickel, Barium, Calcium, Lead, Magnesium and Cadmium Acetates.—These were obtained by recrystallization of commercial salts from pure acetic acid followed by drying at 140°.

Mercuric, silver, zinc and bismuth acetates were not recrystallized but were of the best c. p. quality obtainable and were dried to constant weight.

Silver, lead, strontium, calcium, barium, lithium, cesium, magnesium and potassium perchlorates were prepared in the anhydrous state.

The chlorides and bromides of ammonium, sodium and potassium were recrystallized from water and dried to constant weight. The alkali iodides were of the best c. p. quality obtainable. Solutions of these salts in water did not change the P_H of the solvent.

The organic bases, triphenylguanidine, pyridine, diphenylamine, urea and glycine were of the best obtainable quality. They were not further purified.

Experimental

Four indicators were found sufficient to cover the measurements of the entire series of acetates. Their properties are given in Table I. While there are several indicators suitable for concentrations up to 0.001 molar potassium acetate, we were limited at greater concentrations to only a few. To make the comparisons, a series of concentrations of potassium acetate ranging from 0.08 to 0.0001 molar were made. The

TABLE I

INDICATORS USED IN COMPARISON OF ACETATES IN ACETIC ACID

Indicator	Color change Acid color	 Basic color	Useful range in KAc, concn., *N*
Dimethylamino-azo benzene	Red	Yellow	0–0.0001
Sulfon orange	Violet	Yellow	0.0001–0.001
Cresol red	Yellow	Violet	0.0006–0.008
Tetrabromophenol-tetrachlorosulfonphthalein	Colorless[a] Pink[b]	Yellow	0.002 –0.08

[a] Weakly acid. [b] Strongly acid.

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(1) From the experimental part of a thesis submitted by A. Willman to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1933.

(2) N. F. Hall, THIS JOURNAL, **52**, 5115 (1930).

(3) I. M. Kolthoff and A. Willman, *ibid.*, **56**, 1007 (1934).

results of the colorimetric readings should be accurate to within 5 or 10%.

The results of the conductimetric and colorimetric measurements are given in Table II. Column 4 gives the concentration of potassium acetate in which the color of the indicator is the same as in the 0.02 molar acetate solution investigated. The last column gives the specific conductances of the potassium acetate solutions (at 25°) which impart the same color to the indicator as the 0.02 molar solutions of the other acetates (therefore the last column gives the specific conductance of potassium acetate solution of a concentration corresponding to that given in column 4).

TABLE II

BASICITY OF INORGANIC ACETATES (CONDUCTANCE AND COLORIMETRIC AT 25°)

No.	Acetate	Indicator	Equi-colored solution of $KAc_{norm.}$	Equiv. cond. 0.02 molar soln.	Spec. cond. 0.02 mole soln. × 10^7	Spec. cond. × 10^7 of KAc sol. of concn. in column 4
1	Potassium	T.brt.cl[a]	0.02	0.1217	24.3	24.3
2	Ammonium	T.brt.cl	.015	.1014	20.3	19
3	Anilinium	T.brt.cl	.016	.0988	19.8	19
4	Barium	T.brt.cl	.0088	.0787	15.7	13
5	Sodium	T.brt.cl	.0095	.0646	12.9	13
6	Lithium	T.brt.cl	.0085	.0587	11.7	12
7	Strontium	T.brt.cl	.004	.0554	11.1	8.4
8	Manganese	C.r[b]	.003	.0212	4.23	7
9	Magnesium	C.r	.0011	.0204	4.08	3.9
10	Nickel	C.r	.0015	.0182	3.63	4.7
11	Cadmium	C.r	.00034	.0140	2.80	1.8
12	Bismuth	C.r	.00020	.0103	2.05	1.5
13	Lead	C.r	.00026	.00857	1.71	1.7
14	Urea	S.o[c]	.00003	.00185	0.37	0.45
15	Diphenylamine	S.o	.00005	.00167	.33	...
16	Mercuric	D.y[d]	.0000075	.00096	.19	...

[a] T.brt.cl = Tetrabromophenoltetrachlorosulfonphthalein. [b] C.r = cresol red. [c] S.o = Sulfon orange. [d] D.y = Dimethylaminoazobenzene.

In Table III the equivalent conductances of solutions of some other compounds at 25° are given.

TABLE III

EQUIVALENT CONDUCTANCE OF SOME BASES AT 25°

Compound	Concn., molar	Equiv. cond.
Potassium acetate	0.02	0.1217
2,4-Dichloroaniline	.02	.00365
p-Chloroaniline	.02	.0509
Triphenylguanidine	.02	.373
Pyridine	.02	.1536
Glycine	.02	.1257
Sodium benzoate	.02	.0720
Sodium salicylate	.02	.0733
Silver acetate	.003[a]	.0052
Potassium acetate	.003	.236

[a] On account of the slight solubility of silver acetate a 0.003 molar solution was used.

It may be mentioned that the conductance of all electrolyte solutions in acetic acid increases very strongly with the temperature; changes of 3 to 5% per degree difference of temperature being found.

Discussion of the Results

1. Ammonia which in aqueous solution combines only partly with water is forced to behave like a strong base in the solvent acetic acid. Since the sizes of the ammonium and potassium ions are about the same, potassium and ammonium acetates in acetic acid behave like bases of approximately the same strength.

2. The dissociation of the monovalent inorganic acetates in acetic acid decreases with decreasing ionic size, the order being Cs > K > Na > Li. Silver acetate is much weaker than lithium, which is to be attributed to the strongly deforming effect of silver ions and their ability to form complexes. The dissociation of the alkali earth acetates decreases also with decreasing ionic size, the order being Ba > Sr > Ca > Mg. With the other divalent cations given in Table II, the deforming effect must be considered as well (especially with mercury and lead). The influence of the size of the cation upon the ionization of the base is also clearly shown by organic bases. Pyridine, triphenylguanidine and many other organic bases (see Hall[2]) are strong electrolytes in acetic acid. Therefore the ionization of these strong organic bases is comparable to that of inorganic acetates; the dissociation increasing with increasing size of the cation: NH_4 < Pyridinium < Triphenylguanidinium.

The behavior of glycine is interesting but not unexpected. Since acetic acid (as compared with water) is such a strong acid and a weak base, an amphoteric compound or a hybrid ion such as glycine is forced to behave as a strong base in the former solvent. The strength of the acid group of glycine is of the same order as that of acetic acid, and therefore it can hardly develop its acid properties in this solvent. Therefore glycine dissolved in acetic acid is present as $COOH\text{-}CH_2NH_3^+Ac^-$. The dissociation of this base is of the same order as that of potassium acetate.

3. From the results on the dissociation of inorganic acetates it may be inferred that the acid strength of the cations in acetic acid increases with decreasing size and increasing valence

of the ion. In agreement herewith it was found that the acidity of the rare gas type ions increases in the order $Cs^+ < K^+ = NH_4^+ < Na^+ < Li^+ < Ba^{++} < Sr^{++} < Ca^{++} < Mg^{++}$. Ammonium salts are less solvated than sodium salts in acetic acid, whereas in water the sodium ion is practically neutral and the ammonium ion is a weak acid. Still more striking is the behavior of the pyridinium ion, which in water is a relatively strong acid, whereas in acetic acid it is less acid than the potassium ion.

In connection with the above it is evident that the strong electrolytes which do not change the reaction of water (so-called neutral salts) no longer will show a similar behavior in acetic acid. From the results of a previous study[3] it was inferred that strong electrolytes are partly present as ions and partly as ion-pairs in acetic acid, even at great dilutions. Considering the relatively high equivalent conductances of solutions of perchloric acid as compared with those of all other strong electrolytes, it may be concluded that this acid is more completely ionized than the alkali acetates for example. If this is true, all perchlorates should develop an acid reaction in glacial acetic acid. This was shown to be the case. With 0.002 molar solutions of alkali perchlorates the acidity as measured with thymol benzein decreased in the order $Li > Na > NH_4 = K$. Cesium perchlorate did not change the color of the indicator in the pure solvent; however, the salt is so slightly soluble that no definite conclusions can be drawn from this experiment. The perchlorates of the divalent cations and of silver were much more acid than lithium perchlorate. This is clearly illustrated by the following experiments.

Solutions containing 2×10^{-5} mole of anhydrous perchlorates in acetic acid were titrated with sodium acetate until thymol benzein had the same pink color as in pure acetic acid. The following number of equivalents of sodium acetate were used: $Pb(ClO_4)_2$ 1.26 $\times 10^{-5}$, $Ca(ClO_4)_2$ 0.56 $\times 10^{-5}$, $AgClO_4$ 0.36 $\times 10^{-5}$, $Sr(ClO_4)_2$ 0.22 $\times 10^{-5}$, $LiClO_4$ 0.009 $\times 10^{-5}$.

From the experimental work in this and the previous paper it may be inferred that with the same cation, the acid reaction of a salt will decrease in the order $ClO_4^- > I^- > Br^- > Cl^- > NO_3^-$. Actually it was shown that the potassium salts of these anions have a decreasing acidity in the order mentioned. In 0.002 molar solutions of these salts the color of thymol benzein was more acidic than in pure acetic acid, with the exception of potassium nitrate (the nitrate ion is the strongest base of all the anions considered). The 0.002 molar solution of potassium nitrate imparted the same color to sulfon orange as 0.0007 molar potassium acetate. The acidity of 0.002 molar potassium chloride corresponded to that of 10^{-5} molar, the color of 0.002 molar potassium bromide to that of 2×10^{-5} molar perchloric acid (or 9×10^{-5} molar hydrochloric acid). It is desirable to study the acidity ($P_{H_{HAc}}$) of salts by means of the potentiometric method because important conclusions can be derived in connection with the relation between the strength of the acid and base of the salt. The colorimetric method is less useful for this purpose owing to large salt effects upon the dissociation equilibria. Nevertheless, the above experiments, carried out at approximately the same ionic strengths, show that the generalizations derived are correct. However, it is not permissible to draw any definite conclusions with regard to the absolute acidities of the solutions.

Summary

1. The dissociation of inorganic acetates in acetic acid is a function of the size and the charge of the cation; the dissociation decreases with decreasing size and increasing charge of the cation.

2. The acid strength of cations in acetic acid increases with decreasing size and increasing charge of the ion.

3. Salts which do not change the reaction of water undergo solvolysis in acetic acid. The acidity of the potassium salts of the following inorganic acids decreases in the order $ClO_4^- > I^- > Br^- > Cl^- > NO_3^-$, potassium nitrate being more alkaline than acetic acid.

Salts having a common anion show decreasing acidity in the order $Mg^{++} > Ca^{++} > Sr^{++} > Ba^{++} (> Ag^+) > Li^+ > Na^+ > NH_4^+ = K^+ > Rb^+$.

4. Glycine in acetic acid behaves like a strong base. Its dissociation is of the same order as that of potassium or ammonium acetate.

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