$AgNO_3$ which later redissolved during the ethylene absorption. At higher than 4 *M* the precipitate did not completely redissolve.

Many fluoroborate salts, as well as HBF_4, were observed to increase the ethylene absorption efficiency of $AgBF_4$ to varying degrees. A hypothesis was developed that the effect of HBF_4 and metal fluoroborates is related to their tendency to decrease the hydration of silver ion.[13] In concentrated solutions highly-hydrated cations compete with silver for the water of the solution and thus lower the degree of hydration of silver ion, making it more available for complexing with ethylene. If this hypothesis is correct, the effectiveness of various cations should increase with their tendency to hydrate. We found this to be so. The charge-to-radius ratio for a cation is a good measure of its tendency to hydrate. In Fig. 3 the charge-to-radius ratios for seven cations are plotted *vs.* the ethylene absorption efficiency for 2 *M* $AgBF_4$ containing 2 *M* of the added metal fluoroborate. With the exception of calcium, the agreement is excellent. HBF_4 constitutes a special case that cannot be plotted because of the peculiar significance of the radius of the unsolvated hydrogen ion. The effectiveness of the various cations in increasing ethylene absorption also correlates with Glueckauf's individual ion hydration numbers.[14]

Several attempts were made to determine the effect of added $Be(BF_4)_2$ on the absorption efficiency of $AgBF_4$. However, even when only 0.5 *M* $Be(BF_4)_2$ was used, a large amount of a granular precipitate, slightly gray in color, appeared on mixing the solutions.

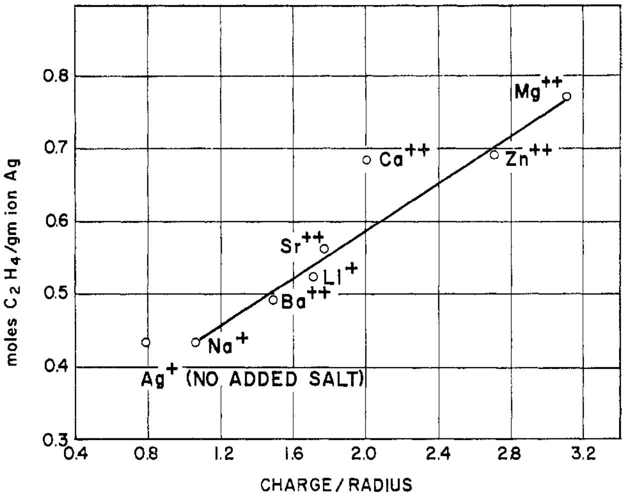

Fig. 3.—Relation between ethylene absorption of aqueous $AgBF_4$ solutions and charge-to-radius ratio of cations of added metal fluoroborate. Each solution was 2 *M* in both $AgBF_4$ and added metal fluoroborate.

The different effect of the presence of HBF_4 and HNO_3 in $AgNO_3$ is interesting. The presence of 4 *M* HBF_4 in 2 *M* $AgNO_3$ increases the efficiency from 0.28 to 0.58 mole of ethylene per gram-ion of silver, but the presence of 4 *M* HNO_3 increases the efficiency to only 0.32. Apparently, the desirable influence of the relatively highly hydrated hydrogen ion is nearly balanced by the opposing effect of an increase in association of silver ion brought about by the excess nitrate.

In a single experiment, H_2SiF_6 was observed to have an influence on the absorption efficiency comparable to HBF_4.

Acknowledgments.—The author is grateful to Dr. D. A. Vassallo of Du Pont and to Professor L. B. Rogers of Purdue University for helpful discussions regarding the mechanism of the interactions, and to Mr. W. P. Pickhardt for performance of some of the experiments.

---

[13] Previous workers have suggested that the hydration of silver ion interferes with the formation of silver–olefin bonds and postulated that differences in the stability constants for silver complexes with isomeric butenes may be due to steric effects involving hydrated Ag^+. See F. R. Hepner, K. N. Trueblood, and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 1333 (1952).

[14] E. Glueckauf, *Trans. Faraday Soc.*, **51**, 1235 (1955).

Contribution from the Departments of Chemistry, Southwestern College,
Winfield, Kansas, and Kansas State University, Manhattan, Kansas

The Dissociation of Metal Acetates in Anhydrous Acetic Acid

By ORLAND W. KOLLING and JACK L. LAMBERT

Received August 8, 1963

The glass–calomel electrode pair was used in a concentration cell at 25° to determine the mode of electrolytic dissociation of fifteen representative mono-, di-, and trivalent metal acetates in anhydrous acetic acid and to evaluate dissociation constants of these solvo-bases. The primary ion separation equilibrium for divalent metals of periodic group IIA and of the first transition series is $M(OAc)_2 \rightleftarrows MOAc^+ + OAc^-$. When arranged in order of decreasing dissociation for acetates of monovalent and divalent metals, the sequence is identical with the "natural order" of stabilities for coordination complexes of the same metals in aqueous media.

The formation constants of coordination complexes in solution for metals in the same oxidation state can be arranged in an empirical sequence demonstrating the relative stabilities for complexes containing a common ligand, and this sequence is largely unchanged with a change of donor group.[1] This so-called "natural order" of stabilities requires that the standard entropy change for complex formation in solution be independent

---

[1] F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 16.

TABLE I
ANALYTICAL RESULTS

Compound	Calcd., %	Found, %
$Ba(OAc)_2 \cdot 2HOAc$	Ba 36.6	Ba 36.6
$Cd(OAc)_2$	Cd 48.8	Cd 47.0
$Ca(OAc)_2$	Ca 25.3	Ca 25.8
$Cr(OAc)_3$	Cr 22.7	Cr 23.1
$2Co(OAc)_2 \cdot HOAc$	Co 28.5	Co 29.7
$Cu(OAc)_2 \cdot HOAc$	Cu 26.3	Cu 27.8
$Fe(OAc)_3 \cdot HOAc$	Fe 19.0	Fe 20.1
$Pb(OAc)_2$	Pb 63.8	Pb 61.9
LiOAc	Li 10.4	Li 10.4
$Mg(OAc)_2 \cdot HOAc$	Mg 12.0	Mg 11.9
$2Ni(OAc)_2 \cdot HOAc$	Ni 28.4	Ni 28.6
KOAc	K 39.9	K 39.5
RbOAc	Rb 60.8	Rb 61.1
NaOAc	Na 28.1	Na 27.5
$Sr(OAc)_2$	Sr 42.6	Sr 41.8

of the metallic ion, and, according to the ligand field treatment of the metals of the first transition series, the order reflects the sequence of inner-orbital stabilization energies.[2] However, the order of stabilities of the complexes has been deduced exclusively from constants obtained for solutions in which a ligand displaces water from the aquo-ion of the metal, either in aqueous solutions or in water-containing binary solvents. Therefore, it seemed desirable to determine the stability sequence in an anhydrous nonaqueous solvent forming solvated ions and having a lower dielectric constant than water. An appropriate system for investigation is the dissociation of solvo-bases in anhydrous acetic acid, since numerous solvates have been characterized and only weak electrolytes are observed.

The potentiometric method reported previously by Kolling[3] was applied to the dissociation of acetates of representative metals in periodic groups IA and IIA and to acetates of metals in the first transition series. The glass and calomel electrodes were used in a concentration cell to determine the type of electrolytic dissociation occurring for these bases. Sodium acetate was the reference base[4] for the comparative evaluation of the dissociation constants of the acetates.

Experimental

Preparation of Anhydrous Acetates.—No single synthetic approach was successful for making completely anhydrous acetates for all of the metals considered. One to ten millimole portions of starting material were used in each of the following methods. Analytical results obtained by classical gravimetric methods[5] are given in Table I.

(A) **Dehydration of Reagent Grade Acetates.**—Commercially available acetates of the elements of periodic group IA and cadmium, copper(II), cobalt(II), lead(II), and nickel(II) were treated with 40 ml. of a 1:3 (v./v.) mixture of acetic anhydride in acetic acid. The solution was heated just below the boiling point for 3 hr., then evaporated to near dryness, and the product was recrystallized from anhydrous acetic acid.

Manganese(II) acetate was prepared by adding the stoichiometric amount of acetic anhydride to the tetrahydrate dissolved in acetic acid and allowing reaction to occur at room temperature for 3 weeks. Any heating of manganese(II) acetate solutions in acetic acid produced a brown suspension of oxidation products.

(B) **Solvolysis of Carbonates.**—Samples of reagent grade carbonates of periodic group IIA metals were suspended in 40 ml. of glacial acetic acid and heated at the boiling point until dissolved (over 8 hr. for strontium carbonate). Five ml. of acetic anhydride was added to the resulting solution, and the remainder of the procedure was that used in method A.

(C) **Dehydration of Impure Basic Acetates.**—Portions of basic acetates of uncertain composition for iron(III) and chromium(III) were partially dissolved in acetic acid by heating at the boiling point for 10 hr., and the remaining residue (about 5–10% of the original samples) was removed by filtration. The filtrate was dehydrated and the product recrystallized according to method A.

(D) **Ion Exchange Followed by Neutralization.**—One mmole of rubidium chloride was converted to RbOH by elution through Amberlite IRA-401 resin in the base form. The eluent was treated with excess acetic acid, evaporated to near dryness, and anhydrous RbOAc was obtained by method A.

The solid metal acetates were dried overnight in a vacuum desiccator containing magnesium perchlorate. Drying at room temperature was used in order to avoid possible pyrolysis occurring at elevated temperatures.

Reagent grade acetic acid, containing 0.1 to 0.2% water by Karl Fischer titration, was made anhydrous by adding the stoichiometric amount of acetic anhydride to consume the water present. After standing 3 weeks, the water content of the acetic acid used in all solutions did not exceed the Karl Fischer reagent blank, equivalent to 0.00054%.

Standardization of Solutions.—Stock solutions of the acetates were in either the 0.01 or 0.1 M concentration range depending upon the solubility of the acetate at 25°. For those solutions that could be standardized by potentiometric titration with perchloric acid, the procedure of Casey and Starke was followed.[5] All titration equivalence points were calculated from the second derivative of potential difference witn respect to volume increment. The acetates of chromium(III) and iron(III) were too weakly basic to permit titration; consequently, their solution concentrations were computed from the weights of the anhydrous solutes.

Potential Difference–Dilution Measurements.—The e.m.f. values for the glass–calomel electrode pair immersed in solutions of known concentration were determined by the method reported in the preceding paper.[3] However, a Leeds and Northrup Model 7401 pH meter was used in this work with the result that the improved over-all precision in the e.m.f. measurements was ±1.0 millivolt or less. Four to six e.m.f. values were obtained on each solution. The potentials were recorded directly without comparing them to sodium salicylate as before[3] since all computations were made using a 0.001 M sodium acetate standard.

Results

The slope for the plot of the logarithm of the concentration of base *vs.* e.m.f. of the glass–calomel electrode pair in acetic acid is determined by the number of ions formed by the dissociation of the base.[6] In Fig. 1 the dilution curves for the acetates of the multivalent cations are shown. For the divalent metals, the linear plots have slopes corresponding to 29.5 ± 0.5 mv. per tenfold change in concentration of base, and the principal dissociation of these acetates in anhydrous acetic acid is according to eq. 1. Iron(III) acetate behaves as a 1:1 weak electrolyte also. The slope of the

$$M(OAc)_2 \rightleftharpoons MOAc^+ + OAc^- \qquad (1)$$

---

(2) P. George and D. McClure, *Progr. Inorg. Chem.*, **1**, 438 (1959).

(3) O. W. Kolling, *Inorg. Chem.*, **1**, 561 (1962).

(4) S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2974 1956).

(5) A. Casey and K. Starke, *Anal. Chem.*, **31**, 1060 (1959).

(6) T. Higuchi, M. Danguilan, and A. Cooper, *J. Phys. Chem.*, **58**, 1167 (1954).

TABLE II

DISSOCIATION CONSTANTS OF METAL ACETATES IN ANHYDROUS ACETIC ACID AT 25°

Acetate of	E_{B_1}, mv.	pK_B
Barium	390	6.48
Cadmium	421.25	7.54
Calcium	398.5	6.77
Chromium(III)	362	5.03
Cobalt(II)	422.0	7.56
Copper(II)	431.5	7.90
Iron(III)	381	6.17
Lead(II)	421.5	7.55
Lithium	399	6.78
Magnesium	412	7.22
Manganese(II)	421.0	7.53
Nickel(II)	424	7.63
Potassium	379	6.11
Rubidium	377	6.04
Sodium	393	6.58[a]
Strontium	395	6.65

[a] Literature value used as the standard pK_{B_2}.[4]

graph for chromium(III) acetate is 20 mv. per tenfold concentration change, indicating the dissociation in eq. 2. The ionization of the acetates of periodic group IA metals as 1:1 weak electrolytes in acetic acid was confirmed, but their lines were not included in Fig. 1.

$$Cr(OAc)_3 \rightleftarrows CrOAc^{+2} + 2OAc^- \qquad (2)$$

The negative logarithm of the dissociation constant (as a concentration constant) for each metal acetate was calculated from eq. 3, which was derived earlier.[3]

$$pK_{B_1} = pK_{B_2} + \frac{2F}{RT}(E_{B_1} - E_{B_2}) \qquad (3)$$

The reference base (NaOAc) is B2, and the e.m.f. values, E_{B_1} and E_{B_2}, are determined graphically from Fig. 1 at $C_B = 0.001$ *M*. The uncertainty in the individual pK_B values in Table II is of the same order of magnitude as that for the sodium acetate standard (±0.02), with the exception of the acetates of lithium, cadmium, copper(II), nickel(II), and iron(III) having ranges of ±0.03 unit. The constants for cadmium acetate and lead acetate were redetermined with recrystallized solutes, since the water content of the glacial acetic acid was nearly 200 times greater in the earlier work.[3]

From the pK_B values in Table II, the orders of increasing dissociation of the acetates in anhydrous acetic acid are: monovalent metals, Li < Na < K < Rb; divalent metals, Cu < Ni < Co < Pb < Cd < Mn < Mg < Ca < Sr < Ba; trivalent metals, Fe < Cr. When viewed as a stability sequence for formation of the uncharged species of the monovalent and divalent metal acetates, the order is the same as the "natural order" found in aqueous systems involving other ligands.[1] Iron(III) and chromium(III) are reversed compared to their behavior in aqueous media; however, it is noted above that $Fe(OAc)_3$ dissociates as a 1:1 electrolyte and $Cr(OAc)_3$ as a diaceto base in acetic acid. Although the stability order of Mn(II) < Cd(II) < Pb(II) is discernible from Table II, it is recognized that the constants are quite close in magnitude and their uncertainties are overlapping.

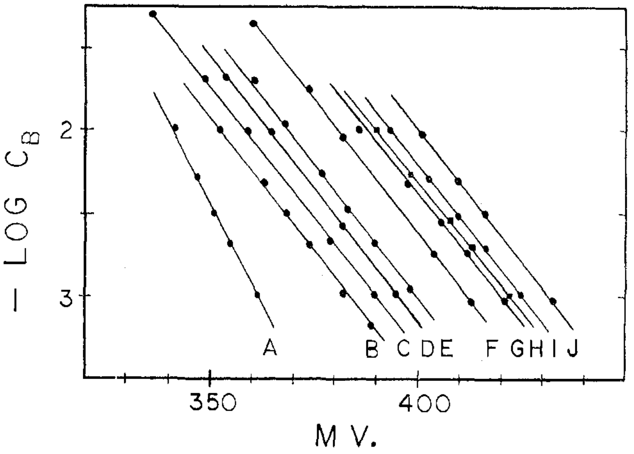

Fig. 1.—The potential difference between the glass–calomel electrode pair as a function of the molarity of the solution at 25°. The curves are: A, $Cr(OAc)_3$; B, $Fe(OAc)_3$; C, $Ba(OAc)_2$; D, $Sr(OAc)_2$; E, $Ca(OAc)_2$; F, $Mg(OAc)_2$; G, $Mn(OAc)_2$; H, $Co(OAc)_2$; I, $Ni(OAc)_2$; and J, $Cu(OAc)_2$.

Discussion

Only a very limited number of results that can be compared directly to those in Table II have been reported by other investigators. The constants (pK_B values) obtained potentiometrically by Bruckenstein and Kolthoff,[4] using the chloranil–calomel electrode pair, agree closely: LiOAc, 6.79, and KOAc, 6.10. The experimental uncertainty in the potentiometrically determined constants is much less than in those computed from conductance measurements,[7] and the latter appear to be less reliable.

In the spectrophotometric study by Proll and Sutcliffe,[8] the influence exerted by colorless acetates upon the 565 mμ absorption band in acetic acid solutions of $Co(OAc)_4^{-2}$ was used to calculate indirectly the dissociation constants of several bases. For the acetates of periodic group IA metals, only the value of LiOAc, 6.80, is in agreement with the potentiometric results in Table II, and the sequence for increasing dissociation reported by these workers is a random one quite different from ours. The values given by Proll and Sutcliffe for the acetates of group IIA metals and $Mn(OAc)_2$ are in the same order of decreasing dissociation as is listed above (Ba > Sr > Mg > Mn), but the dissociation of these diaceto bases is stated to be as 1:2 electrolytes. The disagreement between the two sets of data and the differing mechanism of ion separation for the acetates of the divalent metals cannot be easily rationalized. However, it may be that the cobalt(II) acetate complex functions in the same manner as an acid–base indicator in glacial acetic acid—namely, the indicator absorbance is determined by the stoichiometric concentration of the colorless acid or base, whereas the indicator electrode responds to the hydrogen ion (or acetate ion) activity in anhydrous acetic acid.[9]

The kinetic rate constants for the reaction of divalent

---

(7) M. Jones and E. Griswold, *J. Am. Chem. Soc.*, **76**, 3247 (1954).

(8) P. Proll and L. Sutcliffe, *Trans. Faraday Soc.*, **57**, 1078 (1961).

(9) I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **79**, 1 (1957).

transition metal perchlorates with a substituted porphine base in glacial acetic acid (containing 0.05% water) exhibit an order of decreasing strength as Lewis acids in which Cu > Co > Ni > Mn.[10] This sequence is very similar to the corresponding order of stability of the acetates given above.

The formation constants for the $MOAc^+$ species in aqueous solutions of periodic group IIA elements conform to the same stability sequence as the uncharged acetate in acetic acid,[11] Mg > Ca > Sr > Ba. This is consistent with the conclusion of George and McClure[12] that the relative contribution made by the oxygen atom in the ligand to the stabilization energy is essentially the same in aquo and carboxylate complexes.

Acknowledgment.—We are indebted to the National Science Foundation for financial support of this investigation, under the Research Participation for College Teachers program, NSF GE-350, at Kansas State University.

---

[10] E. Choi and E. Fleischer, *Inorg. Chem.*, **2**, 94 (1963).

[11] G. Nancollas, *J. Chem. Soc.*, 744 (1956).

[12] P. George and D. McClure, *Progr. Inorg. Chem.*, **1**, 451 (1959).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CONNECTICUT, STORRS, CONNECTICUT

Structure Relations in Mixed Metal Oxides

BY LEWIS KATZ AND ROLAND WARD

Received July 25, 1963

The layer model for complex metal oxides is used for cases in which oxygen and large cations are essentially close packed and in the ratio of three oxygens to one large cation. The relationships between various layer sequences and the stoichiometry of the compounds, cation interactions, and octahedral site vacancies are discussed. A twelve-layer model for compounds $A_4^{II}Re_2B^{II}O_{12}$ is consistent with the arguments advanced and with the experimental evidence so far obtained.

Introduction

Framework Picture of ABO_3.—In the synthesis of ternary oxides, we have been concerned mainly with compounds containing both large and small cations. The most usual structure among these is the perovskite type with the ideal formula ABO_3 where A is the large cation and B the small cation. The structure may be regarded as derived from the ReO_3 structure in which the B cations are at the corners of the cube; the A cations occupy the body centers. This is a useful way to look at the structure, because in many compounds deficiencies in A cations and to some extent in oxygen may occur, but deficiencies in B cations are not found.

Layer Picture of ABO_3.—For the purpose of this paper, however, it will be more convenient to consider the structure as derived from the close packing of layers of composition AO_3 (Fig. 1). The A cations may be thought of as lying at the corners of the basal plane of a hexagonal cell with oxygens on the edges and in the face center. Close packed stacking of these layers leads to the formation of one octahedron of oxygens for each AO_3 unit. With cubic stacking, these octahedra share corners; with hexagonal stacking, they share faces.

Cubic Closest-Packed Stacking Only

The hexagonal cell for cubic closest-packed stacking is shown in Fig. 2. Two cubic cells are outlined. A cube body diagonal is in the hexagonal *c*-axis direction. The contents of the hexagonal 110 plane are shown in Fig. 3. A diagrammatic representation of this simple perovskite structure is shown in Fig. 4. The packing, cubic with layer sequence *xyz*, is given at the left (*x*, *y*, *z* are used to designate the layers rather than the usual *A*, *B*, *C* to avoid confusion with the cation designations). In the middle of the figure the occupancy of the octrahedral sites with B cations is indicated. The letter "c" is used to designate a "cubic" layer, *i.e.*, a layer for which the two neighboring layers are of different types (*x* and *y*, *y* and *z*, or *x* and *z*). The letter "h" will be used to designate a "hexagonal" layer, a layer for which the two neighboring layers are of the same type (both *x*, both *y*, or both *z*). The sequence of B cations is also shown at the right of the figure as they appear in the 110 plane of the corresponding hexagonal cell. With cubic close packing the B cations lie on a diagonal line corresponding to the cubic axis of the crystal. The hexagonal unit cell consists of three AO_3 layers. Forms of lower symmetry (orthorhombic, rhombohedral, tetragonal. . .) may be regarded as more or less slight modifications of this ideal structure.

Two Different B Cations.—The introduction of two different B cations in the same phase is facilitated by a large difference in charge of the two ions. This may occur at definite compositions in most cases fixed by stoichiometry. The widest variation is possible when the B cations have an average valence of four. Many compounds have been made corresponding to the formulas (a) $A^{II}_2B^{I}B^{VII}O_6$, (b) $A^{II}_2B^{II}B^{VI}O_6$, (c) $A^{II}_2B^{III}B^{V}O_6$, but few have been prepared where both B cations are tetravalent. The structure adopted