was drained off and the wet crystals further desiccated to remove surface moisture.

Dry beryllium and magnesium carbonates were dissolved in chloric acid solution for the preparation of the chlorates.

Attempts to prepare manganous and chromic chlorates met with failure because of formation of manganese dioxide and chromic acid even at 0°.

By reactions of the hydroxides of Be^{+2}, Ca^{+2}, Sr^{+2}, Al^{+3}, Ga^{+3}, In^{+3}, Hg^{+2}, and Pb^{+2} with excess chloric acid solution to obviate hydrolysis products, these metal chlorates were prepared. (Filter paper and organic solvent should not be brought in contact with chlorates.) The Be^{+2} and In^{+3} chlorates prepared by this technique were not crystalline. They desiccated to glassy solids and were unsuited for measurements. The method used in the preparation of the hydrated metal chlorates yields crystals of the salts with the degree of hydration shown in Table I.

The measurable values of Cl^{35} pure quadrupole resonance of chlorates at room temperature and liquid nitrogen temperature are given in Table I. Resonance frequencies were sought but not found for the chlorates of Li^+, Rb^+, Cs^+, Be^{+2}, Hg^{+2}, In^{+3}, Tl^+, Nd^{+3}, and Zr^{+4}.

TABLE I

Cl^{35} PURE QUADRUPOLE RESONANCES OF METAL CHLORATES

Salt	Crystal habit[a]	eQq 25 ± 1°	eQq −197°
$NaClO_3$	Cub. or trig.	29.920[19]	30.632[19]
$KClO_3$	Monocl.	28.086[2]	28.953[19]
$Mg(ClO_3)_2 \cdot 6H_2O$	.....	.....	29.885[21]
$Ca(ClO_3)_2 \cdot 6H_2O$	Monocl.	.....	30.11
$Sr(ClO_3)_2$	Rhom.	29.161	29.869[21]
$Ba(ClO_3)_2 \cdot H_2O$	Monocl.	29.399	29.922[23]
$AgClO_3$	Tetr.	28.720	29.430
$Cu(ClO_3)_2 \cdot 6H_2O$	Cub.	29.21	30.064[21]
$Zn(ClO_3)_2 \cdot 4H_2O$	Cub.	30.34	31.001
$Cd(ClO_3)_2 \cdot 2H_2O$	.....	.....	29.893
$Al(ClO_3)_3 \cdot 6H_2O$	Rhom.	29.210	29.86
$Ga(ClO_3)_3 \cdot mH_2O$	.....	29.388	29.832
$Ni(ClO_3)_2 \cdot 6H_2O$	.....	29.682	30.498
$Co(ClO_3)_2 \cdot 6H_2O$	Cub.	.....	30.080
$Pb(ClO_3)_2 \cdot H_2O$	Monocl.	29.233	29.712
$Pt(ClO_3)_4$	.....	.....	30.94

[a] "Handbook of Chemistry and Physics," 40th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1958.

Shimomura, Kushida, and Inoue[24,25] state that the quadrupole resonance frequency of Br^{79} in alkali and alkaline earth metal bromates increases monotonically with the electronegativity[26-28] of the metals. The reported resonance of I^{127} in alkali iodates[29] and of Cl^{35} in alkaline earth chlorate monohydrates[22] also increases monotonically with the electronegativity of the metals. Although the data reported here show rough correlations of this type even though different hydrates and crystal forms are compared, additional data are needed for substantiation and the extension of this correlation to these salts of the other periodic group metals.

Acknowledgment.—The author wishes to acknowledge the cooperation of Stephen L. Moshier, of Flow Corporation, for the design and construction of the super-regenerative spectrometer used in this study.

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[29] F. Herlach, *Helv. Phys. Acta*, **34**, 305 (1961).

CONTRIBUTION FROM THE PLASTICS DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY,
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The Effect of Metal Fluoroborates on the Absorption of Ethylene by Silver Ion

BY BERTSIL B. BAKER

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The addition of fluoroboric acid or metal fluoroborates to aqueous silver nitrate or fluoroborate gives a surprisingly large increase in ethylene absorption. The degree of enhancement by various cations correlates well with their charge-to-radius ratio and may be related to degree of hydration.

Introduction

Metal–olefin complexes have been extensively studied because of interest in their structure[1-6] and are the subject of many patents for the separation of paraffins from olefins. With silver, the nitrate salt has received by far the greatest attention, although the perchlorate has also been examined,[7,8] and the fluoroborate was used in a thermodynamic study.[9] Recent patents[10] show silver fluoroborate and silver fluorosilicate to be several times more efficient than silver nitrate for the absorption of ethylene. Further, the amount of ethylene absorbed per mole of silver nitrate decreases with increasing concentration, while with fluoroborate it increases.

We have noted a surprisingly large increase in the ethylene absorption efficiency of silver nitrate or fluoroborate produced by the presence of fluoroboric acid or metal fluoroborates. The practical aspects of this discovery were disclosed in a recent patent.[11] This

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[1] P. D. Gardner, R. L. Brandon, and N. J. Nix, *Chem. Ind.* (London), 1363 (1958).

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[5] A. W. Francis, *J. Am. Chem. Soc.*, **73**, 3709 (1951).

[6] J. W. Kraus and E. W. Stern, *ibid.*, **84**, 2893 (1962).

[7] A. E. Comyns and H. J. Lucas, *ibid.*, **79**, 4339 (1957).

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[9] H. W. Quinn and D. N. Glew, *Can. J. Chem.*, **40**, 1103 (1962).

[10] H. G. van Raay and U. Schwenk, German Patent 1,027,658 (April 10, 1958), and U. S. Patent 2,913,505 (November 17, 1959).

[11] B. B. Baker and D. F. Knaack, U. S. Patent 3,007,981 (November 7, 1961).

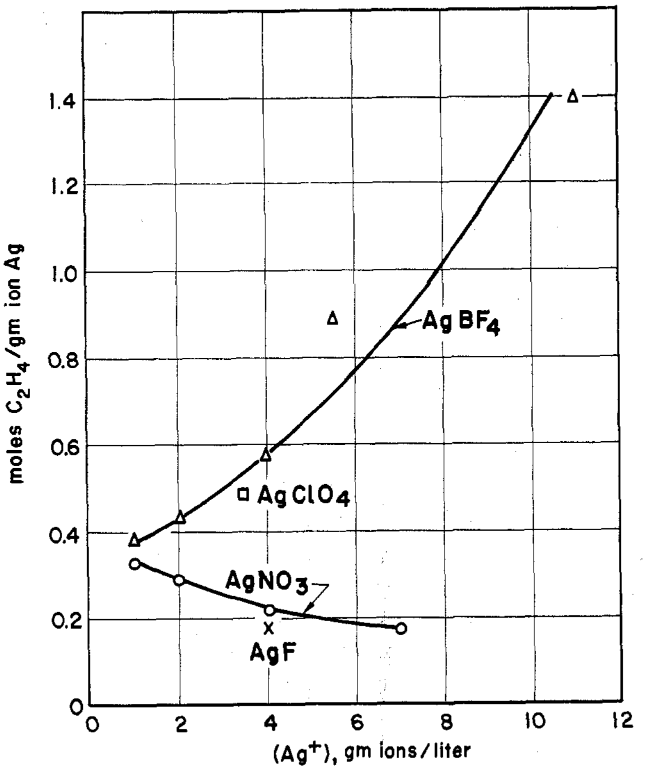

Fig. 1.—Ethylene absorption by solutions of various silver salts.

article will show: (1) that the differences in ethylene absorption by silver nitrate and fluoroborate at various concentrations correlate with the mean activity coefficient of silver ion and (2) that the effects of metal fluoroborates correlate with the charge-to-radius ratio of their cations. This latter correlation supports the hypothesis that the mechanism of the action of the metal fluoroborates is related to their degree of hydration.

Experimental

The $AgBF_4$ used in most of the work was a 47% aqueous solution from General Chemical Division of Allied Chemical and Dye Corporation. Titration with chloride gave a molarity of 3.98, in good agreement with the value calculated from its density of 1.65. However, the solution was quite acid and presumably contained HBF_4, HF, and H_3BO_3. A 7 *M* solution of $AgBF_4$ was made by neutralizing 8 *M* HBF_4 (48–50% aqueous solution, General Chemical or Harshaw Chemical) to pH 5 with solid Ag_2CO_3. Fluoroborates of various other metals were made by addition of their carbonates to this HBF_4. With cations forming insoluble fluorides, such as magnesium, the addition was stopped while the solution was still quite acid (pH of about 1 or 2) to avoid precipitation of the metal fluorides.

The ethylene absorption experiments were done by passing ethylene for 20 min. into 25 ml. of 2 or 4 *M* silver solutions in a weighable glass trap at room temperature. To avoid water loss, the ethylene stream was bubbled first through a $LiNO_3$ solution of appropriate concentration to saturate it with water vapor at about the partial pressure of the solution in the trap. Evaporation losses were then small compared to weight increases due to ethylene absorption, which were usually at least several hundred milligrams. Experiments run for various time intervals demonstrated that 15–20 min. was sufficient to establish a steady state. Since heat is evolved by absorption, temperature was maintained between 22 and 24° by a water bath around the trap.

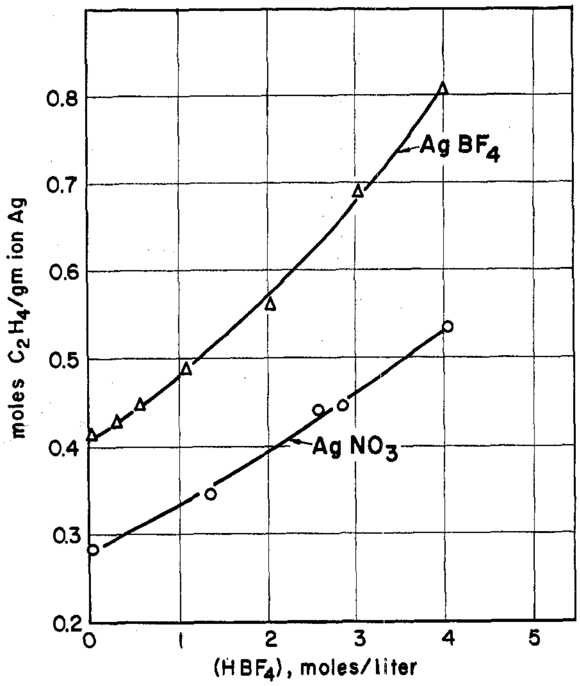

Fig. 2.—Effect of HBF_4 on ethylene absorption by 2 *M* $AgBF_4$ and $AgNO_3$.

Results

Effect of Anion.—Figure 1 gives the results of measurements of the amount of ethylene absorbed per mole of $AgBF_4$, $AgClO_4$, $AgNO_3$, and AgF, all at about 4 *M* concentration. Further, it shows the effect on this molar absorption efficiency of changing the concentration of $AgNO_3$ and $AgBF_4$ from 1 *M* to higher concentrations. The points at 5.5 and 11 *M* on the $AgBF_4$ curve were calculated from data in ref. 9. The mean activity coefficient for $AgNO_3$ decreases with increasing concentration[12] to a value of around 0.3 at 2 *M*. Our own e.m.f. measurements show this decrease to continue to at least 6 *M*. Our measurements for $AgBF_4$ show its activity coefficient to be nearly constant at a value of about 1 between 1.0 and 2.0 *M* and then to rise steeply to a value of about 5 at 6 *M*. Thus the activity coefficient behavior for each salt correlates with the ethylene absorption efficiency shown in Fig. 1.

Effect of HBF_4 and Fluoroborates.—HBF_4 solutions do not absorb a significant amount of ethylene. Figure 2 shows the effect on ethylene absorption efficiency of the presence of HBF_4 in 2 *M* $AgNO_3$ and 2 *M* $AgBF_4$ solutions. It was further found that by employing low molarities of $AgNO_3$ and high molarities of HBF_4 it was possible to exceed 1 mole of ethylene per mole of silver. When 0.16 *M* $AgNO_3$ is made 8 *M* in HBF_4 it absorbs about 1.5 moles of ethylene per gram-ion of silver at room temperature and atmospheric pressure.

It was not possible to go beyond 4 *M* HBF_4 with 2 *M* $AgNO_3$, since any additional HBF_4 caused a precipitate of $AgNO_3$ to appear (X-ray diffraction identification). Even at 4 *M* there was a small amount of

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[12] W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd Ed., Prentice-Hall, New York, N. Y., 1952, p. 354.

$AgNO_3$ 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.

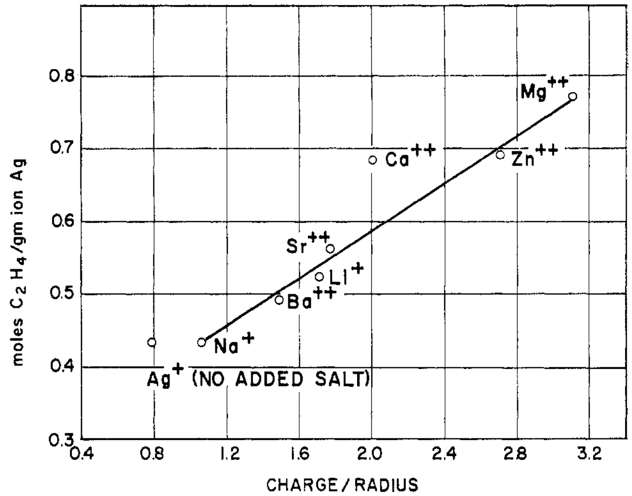

Fig. 3.—Relation between ethylene absorption of aqueous $AgBF_4$ solutions and charge-to-radius ratio of cations of added metal fluoroborate. Each solution was 2 *M* in both $AgBF_4$ and added metal fluoroborate.

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.

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[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,
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The Dissociation of Metal Acetates in Anhydrous Acetic Acid

BY ORLAND W. KOLLING AND JACK L. LAMBERT

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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.