out" the barbituric acid into the interface and thereby increase the effectiveness of the barbituric acid in reducing the surface tension of the water, and the normal tendency of the salt to increase the surface tension of the water. The curves for the surface tension of solution of barbituric acids 1 through 7, the low molecular weight acids as a function of the concentration of salt (see Table I), have positive slopes, and in all of these instances the normal effect of the salt to increase the surface tension of the water is lessened by the presence of the barbituric acid, and to a greater degree as the molecular weight increases. In the case of barbituric acids 8 through 13, the ones with heavy substituent groups, the slopes are negative, showing the salt is actually enhancing the surface tension reducing properties of the barbituric acid.

NASHVILLE 5, TENN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OF THE UNIVERSITY OF MICHIGAN]

The Preparation and Properties of Complex Fluoroarsenates[1]

BY H. M. DESS AND R. W. PARRY

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Potassium dihydrogen arsenate, KH_2AsO_4, reacts with a 48% aqueous solution of hydrofluoric acid to give potassium hydroxypentafluoroarsenate(V), $K[AsF_5OH]$. Potassium hexafluoroarsenate(V), $K[AsF_6]$, can be prepared by the action of liquid anhydrous HF on $KAsF_5OH$ or KH_2AsO_4. The reaction is discussed. Procedures for preparing ammoniun and cesium hexafluoroarsenates and hexafluoroarsenic acid, $HAsF_6$, are described. Cesium hexafluoroarsenate is of low solubility in water while NH_4AsF_6, $HAsF_6$ and $KAsF_6$ are water soluble. The data suggest a means for separating the light and heavy alkali metals.

In the pioneer work on the fluoroarsenates[2-4] products which were assumed to contain the hexafluoroarsenate anion, (AsF_6^-), were produced from an aqueous solution containing KH_2AsO_4 and 48% HF. It was reported that the resulting AsF_6^- ion underwent extensive and ready hydrolysis in water solution to give arsenic oxyfluorides.

In contrast to the foregoing reports the results of Ruff, Stauber and Graf[5] suggest more difficult preparation and hydrolysis of the AsF_6^- ion. The compound $NOAsF_6$ (reported as $NOF \cdot AsF_5$ by Ruff) could not be analyzed for arsenic and fluorine without a preliminary sodium fusion of the sample.[6] Difficult hydrolysis of the AsF_6^- ion is also implied in the recent reports of Woolf and Emeleus.[7] The compounds $KAsF_6$ and $NOAsF_6$ were synthesized by methods involving the powerful fluorinating agent bromine trifluoride. The analytical methods used for identification involved preliminary fusions with a mixture of Na_2CO_3 and $NaNO_3$, not direct hydrolysis in aqueous solution. The current paper is aimed at a resolution of the uncertainty which arises from the early literature on the synthesis and analysis of compounds containing the AsF_6^- ion.

The reaction between 48% aqueous hydrofluoric acid and potassium dihydrogen arsenate produces potassium hydroxypentafluoroarsenate(V), $K[AsF_5OH]$, rather than the hexafluoroarsenate salt, $K[AsF_6]$. Anhydrous HF converts the $KAsF_5OH$ to $KAsF_6$. Both the AsF_5OH^- and the AsF_6^- anions give precipitates with nitron acetate or with tetraphenylarsonium chloride, $[As(C_6H_5)_4]Cl$. Lange[4] used the formation of a precipitate with nitron acetate as evidence for hexafluoroarsenate formation in aqueous solution. He erroneously described his precipitate as nitron hexafluoroarsenate monohydrate.

The $[AsF_5OH^-]$ anion hydrolyzed relatively rapidly in water solution. The process was accelerated by acid, base or heat. In contrast the AsF_6^- ion showed no hydrolysis as a result of (1) boiling a strongly basic solution almost to dryness, (2) storing a strongly basic solution for six weeks at room temperature. Conventional tests for determining As(V) such as reduction with KI or precipitation of As_2S_5 with $(NH_4)_2S$ were unsuccessful when applied to the true AsF_6^- ion. Similarly silver arsenate could not be precipitated by adding silver ion to a solution of $KAsF_6$. In contrast one could easily determine arsenic in $KAsF_5OH$ by taking advantage of its ready hydrolysis in boiling NaOH solution. Reduction of As(V) with KI was easily effected in the hydrolyzed solution. After complete hydrolysis of AsF_5OH^- to arsenate, no precipitate of complex salt was obtained with nitron or tetraphenylarsonium chloride.

The properties of the AsF_6^- ion are seen to be quite similar to those of the PF_6^- ion while the AsF_5OH^- ion is much less stable toward hydrolysis. The failure of aqueous hydrofluoric acid to convert AsF_5OH^- to AsF_6^- and the great stability of the latter toward hydrolysis would seem to indicate that a relatively high energy barrier blocks the exchange reaction between the sixth fluoride and hydroxide ion

$$AsF_5OH^- + F^- \underset{\text{slow}}{\rightleftharpoons} AsF_6^- + OH^-$$

These observations may be rationalized in terms

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[1] Abstracted from a thesis submitted on February 9, 1955, to the Horace H. Rackham School of Graduate Studies of the University of Michigan by H. M. Dess in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] M. C. Marignac, *Ann. chim. phys.*, [4], **10**, 371 (1867); *Ann.*, **145**, 237 (1867).

[3] Gmelin, "Arsen," System-Nummer 17, Verlag Chemie, GMBH, Weinheim, 1952, p. 366.

[4] W. Lange and E. Muller, *Ber.*, **63**, 1058 (1930).

[5] O. Ruff, K. Stauber and H. Graf, *Z. anorg. Chem.*, **58**, 325 (1908).

[6] Ruff noted that AsF_5 presents no special analytical problems but did not speculate further as to the cause of the interference in his new complex.

[7] A. A. Woolf and H. J. Emeleus, *J. Chem. Soc.*, 1050 (1950); A. A. Woolf, *ibid.*, 1053 (1950).

of a mechanism[7a] which is consistent with the general mechanism schemes of Pearson and Basolo.[7a] An HF molecule is coördinated to an acid arsenate ion giving a temporary coördination number of five for arsenic in the transition state. A proton is transferred from a coördinated OH^- ion or HF molecule to another coördinated OH^- ion. The resulting water molecule is displaced by either an HF molecule or a solvent water molecule. With increasing replacement of OH^- by F^- around the As(V) the ability of the complex ion to hold non-ionized protons would diminish (*e.g.*, $HAsF_6$ is a very strong acid, $HAsF_5OH$ is strong, H_3AsO_4 is significantly weaker). Since ionized protons would be less easily available for an internal proton shift, the internal transfer of a proton would be dependent upon the number of OH^- ions bound to the arsenic(V). If two OH^- groups were coördinated in adjacent positions, an easy internal proton transfer would be anticipated. Facile $OH^- \leftrightarrow F^-$ exchange would then be expected. If, however, only a single OH^- remained coördinated, *free* solvent HF molecules would have to serve as proton donor to the coördinated OH^- ion, and as attacking ligand for displacing the water molecule which results from proton transfer. Replacement of the last OH^- should thus be effected by high concentrations of HF. The above argument agrees with the fact that $KAsF_5OH$ is formed in solutions containing up to 50% HF, while $KAsF_6$ is formed in anhydrous HF.

The question of hydrolysis can be treated by reversing the above process. Hydrolysis reactions of halides frequently occur through the initial coördination of a water molecule to the central ion; this process is followed by loss of the acid HX. Such a mechanism would not be applicable to the AsF_6^- ion without the temporary expansion of the coördination number of arsenic to seven. On the other hand, AsF_5OH^- could undergo easier hydrolysis simply by transfer of a proton from the OH^- to F^-, followed by loss of HF.

In addition to $KAsF_5OH$ and $KAsF_6$ the compounds NH_4AsF_6, impure $CsAsF_6$ and crystalline $HAsF_6 \cdot 6H_2O$ were prepared. Solubility relationships among these compounds were of considerable interest. $KAsF_6$ dissolved to the extent of 1.1 moles/l. at 29–30°. The ammonium salt was very much more soluble, and the solid acid crystals melted near room temperature. $HAsF_6$ is a typical strong acid. In contrast to the foregoing, the cesium salt was only slightly soluble in water (0.067 mole/l.). A possible method for separating Cs^+ from K^+ and NH_4^+ would seem to be suggested by the data.

If one compares earlier data of Lange and Askitopoulos[8] with the results of the present study, it is seen that both the hexafluorophosphates and hexafluoroantimonates parallel the hexafluoroarsenates in solubility trends. For a given alkali metal such as potassium, the solubility increases regularly in going from the hexafluorophosphate to the hexafluoroantimonate. Solubilities of the arsenic complexes are no longer anomalous in view of the evidence now available.

Experimental

1. **The Preparation and Analysis of Potassium Hydroxypentafluoroarsenate (V), $KAsF_5OH$.**—A 10–15 ml. quantity of 48% HF was added to 10 g. of KH_2AsO_4 in a polyethylene beaker. After evaporating the resulting solution to dryness on a steam-bath, a white crystalline residue was obtained. The residue was ground, dried at 110–115° and analyzed. A weighed sample (0.5 g.) was dissolved in about 15 ml. of water and about 1 g. of KOH was added. The solution was boiled vigorously for several minutes and diluted to volume. To determine arsenic an aliquot of the unknown was made 6 *M* in HCl, chilled to near 0° and treated with an excess of KI in water. The iodine produced by reduction of As(V) was titrated immediately with standard $Na_2S_2O_3$ solution.

Fluoride was distilled from an aliquot of the unknown solution which had been mixed with an equal volume of concentrated $HClO_4$.[9] The separated fluoride was determined by the lead chlorofluoride method.[10]

Anal. Calcd. for $KAsF_5OH$: As, 33.2; F^-, 42.1. Found: As, 33.3; F^-, 42.2; density $KAsF_5OH$, 2.97 g./ml.

INTERPLANAR SPACINGS AND INTENSITY OF REFLECTIONS FOR $KAsF_5OH$ FROM DEBYE–SCHERRER X-RAY POWDER PATTERNS[a]

4.76 w	2.76 w	2.17 vw	1.93 w
4.30 s	2.62 w	2.10 vw	1.82 vw
3.67 w	2.35 w	2.07 vw	1.79 vw
3.37 ms	2.28 vw	1.99 vw	1.75 w

[a] Copper Kα radiation. Camera circumference, 180 mm.

2. **The Preparation and Analysis of Potassium Hexafluoroarsenate (V).**—About a 60-g. sample of $KAsF_5OH$ (or an equivalent amount of KH_2AsO_4) was placed in the special fluorination apparatus. The apparatus was constructed from a copper tube 3.0 inches long, 2.0 inches in diameter and 0.125 inch wall thickness. The tube was closed at the bottom with a copper disk silver alloy brazed in place. At the top a copper flange and Teflon gasket were fitted with a copper cover plate bolted to the flange in eight places. A copper inlet tube fitted with a small brass-bodied needle valve was silver alloy brazed into the cover plate. The assembled system was evacuated and anhydrous HF from a tank was condensed onto the sample by chilling the copper container to −78° with a Dry Ice–isopropyl alcohol cooling-bath. At least a threefold excess of the HF was taken (as determined by weighing the sealed container before and after the addition). The sealed system was allowed to stand at room temperature for several hours, after which time the excess HF was allowed to evaporate. This was effected by first opening the valve (after disassembling the threaded connection) and then removing the cover plate. The product was subjected to a rapid stream of air in order to drive off the HF and H_2O which resulted from the reaction. The product finally was dried at 110–115°. Purification was effected readily by recrystallization from water solution.

In accord with Ruff's observation, considerable difficulty was encountered in obtaining satisfactory analytical data.

The following methods were used: (1) a weighed sample was carried through the perchloric acid distillation procedure, which destroyed the AsF_6^- complex. Fluoride was determined as previously described, and the uncomplexed arsenic remaining in the stillpot was precipitated as silver arsenate; determination of silver by the Volhard method[11] gave an indirect measure of the arsenic. Arsenic and fluoride both tended to be somewhat low since it was found that small quantities of $HAsF_6$ distilled over undecomposed during the initial heating with perchloric acid. (2) The AsF_6^- ion was determined directly as the insoluble tetraphenylarsonium salt, $[(C_6H_5)_4As](AsF_6)$.[12]

[7a] R. G. Pearson and F. Basolo, THIS JOURNAL, **78**, 4878 (1956); F. Basolo, W. R. Matoush, and R. G. Pearson, *ibid.*, **78**, 4883 (1956).

[8] W. Lange and K. Askitopoulos, *Z. anorg. Chem.*, **223**, 369 (1935).

[9] H. H. Willard and H. Diehl, "Advanced Quantitative Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 369.

[10] W. W. Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, Inc., New York, N. Y., 1939, pp. 74–77.

[11] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 267.

[12] H. M. Dess, R. W. Parry and G. L. Vidale, THIS JOURNAL, **78**, 5730 (1956).

Anal. Calcd. for $KAsF_6$: As, 32.8; F^-, 50.0; total AsF_6^-, 82.9. Found: As, 32.2 ± 0.6; $F^- = 48.8 \pm 0.5$; AsF_6, 82.7 ± 0.5; density $KAsF_6$, 3.29 g./ml.

The X-ray crystallography of $KAsF_6$ has been described by Roof.[13]

3. The Preparation of Ammonium Hexafluoroarsenate.—Two and three-tenths grams of arsenic pentoxide and 13.2 g. of ammonium fluoride were mixed well and fused in a nickel crucible. The ammonium hexafluoroarsenate crystallized from the melt. The product so obtained was contaminated with uncomplexed pentavalent arsenic and nickel salts. The crude material was purified by dissolving it in water and precipitating out all uncomplexed pentavalent arsenic as silver arsenate (silver hexafluoroarsenate is extremely water soluble). The excess silver from the precipitant was removed by adding a small quantity of ammonium chloride solution to the system. A small yield of relatively pure NH_4AsF_6 was obtained by evaporating this solution to near dryness and filtering off the crystals of the product. The material was dried at 110° and analyzed for AsF_6^-; AsF_6^- found, 91.5%; theory, 91.3%.

An adaptation of the procedure described by Palmer[14] for preparing NH_4PF_6 from KPF_6 and $[Cd(NH_3)_6](PF_6)_2$ gave a better synthesis of NH_4AsF_6 than the direct method described above.

4. Preparation of Hexafluoroarsenic Acid.—A solution of $KAsF_6$ was shaken with batches of Dowex-50 ion-exchange resin, in the acid form. The resulting solution of $HAsF_6$ was evaporated under reduced pressure. Eventually large colorless hexagonal crystals came out of solution. These crystals melted around room temperature and an AsF_6^- analysis indicated a composition corresponding approximately to the hexahydrate, $HAsF_6 \cdot 6H_2O$; AsF_6^- found, 65.1%; theory, 63.4%. The phosphorus analog has been reported by Lange.[15]

5. Preparation of Cesium Hexafluoroarsenate.—Impure cesium hexafluoroarsenate was prepared by mixing solutions of $KAsF_6$ and commercial cesium chloride; the cesium salt immediately precipitated. A low analysis for AsF_6^- (observed, 52.5%; theory for $CsAsF_6$, 58.7) was traced to impurities in the product. $2Na_3AsO_4 \cdot NaF \cdot 19H_2O$ and Cs_2SiF_6 were identified as contaminants by Dr. C. E. Nordman using crystallographic methods. More detailed crystallographic data on the cesium and ammonium salts have been collected by Dr. Nordman and will be available in another publication.

Acknowledgments.—The authors wish to thank Dr. H. H. Willard for suggesting the use of tetraphenylarsonium chloride as a precipitant for hexafluoroarsenate. Dr. Thair Higgins and Professor E. F. Westrum, Jr., made available the fluorination apparatus herein depicted, and then aided in its use. Their assistance is gratefully acknowledged. One of the authors (H. M. D.) wishes to express his sincere appreciation to the National Science Foundation for financial support of this work.

ANN ARBOR, MICHIGAN

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(13) R. B. Roof, Jr., *Acta Cryst.*, **8**, 739 (1955).

(14) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge Univ. Press, Cambridge, England, 1955, p. 303.

(15) W. Lange in J. H. Simons, "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., 1950, p. 164.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE CITY COLLEGE OF NEW YORK]

The Mechanism of the Precipitation of Magnesium Oxalate from Supersaturated Solutions. II. The Heat and Entropy of Activation[1]

BY BERNARD LICHSTEIN[2,3] AND FRANK BRESCIA

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The heat and entropy of activation and the entropy change for the over-all reaction have been obtained for the precipitation of magnesium oxalate from its supersaturated solution. The rate of nucleation also has been estimated. The results are interpreted in terms of the previously proposed mechanism.

Introduction

In our previous paper,[4] it was stated that, on the basis of the proposed mechanism of the precipitation of magnesium oxalate from supersaturated solutions, the entropy of activation and the entropy change for the over-all reaction would be of the same order of magnitude. Measurements of the temperature dependence of the rate constant for the precipitation of magnesium oxalate and of the solubility of magnesium oxalate have therefore been made.

The experimental procedures used are essentially the same as previously recorded.[4]

The heat and entropy of activation were calculated from

$$\Delta H^* = \frac{2.30RT_1T_2}{T_2 - T_1} \log \frac{k_2}{k_1}$$

and

$$\Delta S^* = 2.30R \log \frac{kNh}{\kappa RT} + \frac{\Delta H^*}{T}$$

making the usual assumption that $\kappa = 1$. The numerical value of the equilibrium constant, K, at zero strength, for the over-all reaction

$$MgC_2O_4 \cdot 2H_2O \text{ (solid)} = Mg^{++} + C_2O_4^{--} \text{ (aqueous soln.)}$$

was calculated from $K = C^2_{C_2O_4^{--}} \cdot \gamma^2_{MgC_2O_4}$, in which $C_{C_2O_4^{--}}$ refers to the concentration of oxalate in moles per liter in a saturated solution of magnesium oxalate. The solubility was measured as a function of ionic strength and the results were extrapolated to $\mu = 0$, at which condition $\gamma = 1$.

The standard thermodynamic quantities ΔF°, ΔH° and ΔS°, for the over-all reaction as written above, were calculated from the usual equations

$$\Delta F^\circ = -2.30RT \log K$$

$$\Delta H^\circ = \frac{2.30RT_1T_2}{T_2 - T_1} \log \frac{K_2}{K_1}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T}$$

The results are summarized in Table I. The redetermined rate constant at 25.0° agrees within

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(2) The research was carried out while a senior at The City College of New York.

(3) Geochemistry Division, Lamont Geological Observatory, Torrey Cliff, Palisades, New York.

(4) J. Peisach and F. Brescia, THIS JOURNAL, **76**, 5946 (1954).