associated with k_3: $A = 3.69 \times 10^{14}$ sec.$^{-1}$, $E =$ 36.3 kcal./mole. Analogous parameters[17] for k_1 are: $A = 3.90 \times 10^{14}$ sec.$^{-1}$, $E = 34.6$ kcal./mole. The frequency factors and activation energies are reported to three figures solely for purposes of calculation of rate constants at various temperatures from the A and corresponding E. Because of the limited temperature range studied and experimental error it is possible to select a variety of A's and E's that will give an adequate fit.

A theoretical discussion of the relative reactivities of methyl substituted thioureas as well as other thiourea derivatives will be presented in the last paper of this series.

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AUSTIN, TEXAS

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[17] These parameters will reproduce the k_1's (Table IB) with an average deviation of 10%.

[CONTRIBUTION NO. 409 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Fluoroarsenites

BY E. L. MUETTERTIES AND W. D. PHILLIPS

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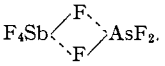
The interactions of several inorganic fluorides with arsenic trifluoride were examined and a physical characterization of some of these systems was made. Some monovalent fluorides formed solids of the composition $MAsF_4$. The stability of these fluoroarsenites appeared to be inversely related to the polarizing power of the cation. Dissociation of the fluoroarsenites was very high in the fused state, and in arsenic trifluoride solution they underwent rapid fluorine exchange. The existence of the tetrafluoroarsenite anion in melts and in solution could therefore not be established by n-m-r data. A bridged structure is suggested for the antimony pentafluoride complex:  $F_4Sb\langle{}^{F}_{F}\rangle AsF_2$.

Introduction

The conductivity of arsenic trifluoride is greatly increased by the addition of potassium fluoride or antimony pentafluoride. Woolf and Greenwood[1] suggested that the compounds which can be isolated from these systems may ionize in solution as

$$KAsF_4 \rightleftarrows K^+ + AsF_4^-$$

$$AsF_3 \cdot SbF_5 \rightleftarrows AsF_2^+ + SbF_6^-$$

This present study was undertaken to gain a more general understanding of the behavior of arsenic trifluoride toward inorganic fluorides and an attempt also was made to determine the structure of the complex fluorides obtained from some of these systems.

Experimental

Materials and Apparatus.—Arsenic trifluoride was stored in contact with sodium fluoride and was distilled (b.p. 60.3° (760 mm.)) prior to use. Commercial samples of the alkali metal and thallous fluorides were used. These fluorides all totaled at least 98% metal and fluorine after vacuum drying at 100–250°. Baker and Adamson antimony pentafluoride was distilled before use. Matheson tank boron trifluoride was stored over sodium fluoride to remove any traces of hydrogen fluoride.

Dissociation pressures were determined in an isoteniscope. With this apparatus, cathetometer readings of the manometer had a precision of ±0.5 mm. which proved to be much better than the reproducibility of the actual dissociation pressures of various samples. The fluorine magnetic resonance spectra were obtained using a Varian high resolution n-m-r spectrometer and electromagnet[2] at a frequency of 30 Mc. and a magnetic field of 7,500 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the fluorine resonance of CF_3COOH. Positive frequency displacements indicate resonances occurring at lower fields than the fluorine resonance of CF_3COOH. Calibration was accomplished by superimposing an audio-frequency on the sweep field to produce side band peaks to the CF_3COOH resonance.[3]

Preparation of Fluoroarsenites.—The fluorides of potassium, rubidium, cesium and thallium all reacted spontaneously and quite exothermally with arsenic trifluoride. Because the products of these reactions had limited solubility in arsenic trifluoride, the fluoroarsenites were prepared in pressure vessels at 80° to ensure complete reaction. Three hour reaction periods proved satisfactory for quarter-mole quantities of the metal fluoride; a 300% excess of arsenic trifluoride was used. The products, which were slurries, were filtered and the solids were recrystallized from arsenic trifluoride.

Anal. Calcd. for $KAsF_4$: K, 20.6; As, 39.4; F, 40.0. Found: K, 19.91; As, 39.21; F, 39.45. Calcd. for $CsAsF_4$: Cs, 46.8; As, 26.4; F, 26.8. Found: Cs, 47.3; As, 26.96; F, 27.06. Calcd. for $TlAsF_4$: Tl, 57.6; As, 21.1; F, 21.4. Found: Tl, 57.61; As, 21.59; F, 20.61.

Lithium and sodium fluorides did not react with arsenic trifluoride. Treatment of these fluorides with liquid arsenic trifluoride at temperatures up to 160° in pressure vessels yielded only the starting materials. Analyses of the solid products showed that less than 1% arsenic was present.

Characterization of the Fluoroarsenites.—All the fluoroarsenites were extremely hygroscopic: 30 seconds exposure to fairly humid air was sufficient to turn tenth-gram quantities of the solids to oils. Water reacted exothermally with the fluoroarsenites to yield clear solutions. The F^{19} magnetic resonance spectra of these solutions consisted solely of a rather broad resonance in the fluoride ion region. There was no evidence for a fluoroarsenite ion, *e.g.*, AsF_4^- or $AsOF_2^-$, in aqueous solution, but such an ion could be present in very low concentration and in equilibrium with fluoride and arsenite ions.

Saturated solutions of the fluoroarsenites in arsenic trifluoride at 30° contained 2% K, 6% Rb, 8% Cs and 11% Tl, respectively. Such solutions had a F^{19} magnetic resonance spectrum that consisted of a single resonance, shifted slightly from that of arsenic trifluoride toward a position denoting higher shielding: δ for AsF_3 = 1050 c.p.s. and δ for $KAsF_4$ in AsF_3 = 1025 c.p.s. The absence of two or

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[1] A. A. Woolf and N. N. Greenwood, *J. Chem. Soc.*, 2200 (1950).

[2] Varian Associates, Palo Alto, California.

[3] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

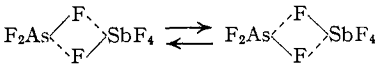
more resonances indicated that fluorine exchange was taking place in this system. (Exchange phenomena of sufficiently high frequency have been shown capable of collapsing a two-line spectrum into a single, concentration-dependent resonance.[4]) The exchange rate was too fast to be "frozen out" by cooling the solutions. It was therefore not possible to establish whether F^- or AsF_4^- is the major conducting species in arsenic trifluoride solution.[5]

The F^{19} magnetic resonance spectrum of a melt of $KAsF_4$ consisted of a single rather broad resonance at +940 c.p.s. The tetrafluoroarsenite anion is isoelectronic with selenium tetrafluoride and thus may be expected to have a trigonal bipyramid structure. The absence of structure in the spectrum of the melt is due to fluorine exchange. The exchange mechanism may be simply described by a dissociation of the fluoroarsenite into AsF_3 and MF. This dissociation was demonstrated tensimetrically at temperatures below the melting points. The dissociation pressures at 100° ranged from 0.18 atm. for $KAsF_4$ to 0.07 atm. for $CsAsF_4$. Equilibria were attained slowly. Because of slight etching of the glass equipment by the fluoroarsenites at 100°, the dissociation pressures are considered to be approximate values.

Covalent Fluorides.—Nuclear magnetic resonance spectra of binary systems of covalent fluorides and arsenic trifluoride were examined in an attempt to gain structural information. Samples were prepared by condensing the fluorides in 5 mm. o.d. Pyrex tubes which were then sealed. Approximately equimolar quantities of the fluorides were used except where excess arsenic trifluoride was necessary to prevent solid formation.

Although boron trifluoride slightly increases the conductivity of arsenic trifluoride, no evidence for interaction of these two liquids was obtained at temperatures up to ~ − 10° or between liquid arsenic trifluoride and gaseous boron trifluoride up to 30°. The characteristic resonances of the components were observed. Woolf and Greenwood[1] have suggested the possibility of an unstable $AsF_2^+BF_4^-$ compound in such mixtures but the n-m-r data give no support to this suggestion.[6]

The F^{19} magnetic spectrum of arsenic trifluoride–antimony pentafluoride consisted of a single resonance peak. The position of the peak was between the resonance positions of the pure fluorides and was concentration dependent. Any type of compound formed between the antimony and arsenic fluorides would have non-equivalent fluorines and would present two or more peaks in the fluorine spectrum. Absence of structure in the spectrum is attributed to a rapid fluorine exchange (low temperature did not slow the rate sufficiently to permit a structural analysis). Although lacking conclusive evidence, a bridge-type structure is suggested for this system in the liquid state since such a structure provides a simple mechanism for fluorine exchange



A bridge structure is supported by related data. Bridge-type structures have been cited as intermediates for fluorine exchange in halogen fluorides.[7] Antimony pentafluoride appears to have bridge-bonding[8] and a bridge intermediate has been proposed for chlorine exchange between antimony (III) and antimony(V).[9] It should be noted that a simple coördination complex $F_5Sb–AsF_3$ is not acceptable as an intermediate for exchange since dissociation of such a complex would not involve cleavage of As–F or Sb–F bonds.

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[4] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

[5] Although the fluoroarsenites are undoubtedly composed of M^+ and AsF_4^- aggregates in the solid state, it does not necessarily follow that the tetrafluoroarsenite anion is the major anion in AsF_3 solution. The equilibrium for AsF_4^-(soln) ⇄ AsF_3 + F^-(soln) may be far to the right.

[6] It should be noted that an $AsF_2^+BF_4^-$ intermediate could be present to concentrations involving approximately 5% of the total fluorine and not be detected. However, if this intermediate is present, rapid equilibration between the components and the intermediate does not occur. Rapid equilibration would yield a single F^{19} resonance rather than the observed, non-perturbed resonances of the components.

[7] E. L. Muetterties and W. D. Phillips, THIS JOURNAL, **79**, 322 (1957).

[8] E. L. Muetterties and W. D. Phillips, manuscript in preparation.

[9] H. M. Neumann and H. Brown, THIS JOURNAL, **78**, 1843 (1956).

WILMINGTON 98, DEL.

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

Di-*t*-butylberyllium and Beryllium Hydride[1]

BY E. L. HEAD, C. E. HOLLEY, JR., AND S. W. RABIDEAU

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Methods are described for the preparation of pure di-*t*-butylberyllium and for the preparation of beryllium hydride (approx. 80 wt. %) by the pyrolysis of both pure di-*t*-butylberyllium and its etherate. Pure di-*t*-butylberyllium is a clear, colorless, mobile liquid with a density of 0.65 g./cc. and a freezing point of −16°. When freshly prepared it has a vapor pressure of about 35 mm. at 25°; on standing it undergoes slow decomposition at room temperature with the evolution of isobutene. Beryllium hydride prepared by pyrolysis of di-*t*-butylberyllium has a density of about 0.57 g./cc., evolves hydrogen slowly at 190 to 200° and rapidly at 220°, is relatively inert to laboratory air, and reacts slowly with water and rapidly with acid. It was analyzed by chemical and microscopic methods. It gave no X-ray pattern.

Introduction

The preparation of beryllium hydride has been announced by a number of workers. In view of the apparently tenuous nature of some of the published results, the present authors, with others,[2] have investigated these procedures in considerable detail. Attempts to prepare beryllium hydride by heating beryllium in atomic hydrogen by the method of Pietsch[3] were unsuccessful. A surface reaction between excess lithium hydride and beryllium chloride in ether solution was observed as described by Wiberg and Bauer,[4] but separation of the product, which contained organic material, from the excess lithium hydride could not be accomplished and analysis was not possible. There seems to be little direct evidence for identifying this material as beryllium hydride.

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[1] This work was done under the auspices of the Atomic Energy Commission.

[2] Some 30 staff members of this Laboratory have contributed to the program to a greater or lesser extent. In addition to procedures mentioned here, preparation of beryllium hydride was attempted by many other methods, including direct combination of the elements under various conditions, reduction of inorganic salts and reduction of beryllium alkyls with various reducing agents. Los Alamos Scientific Laboratory report LA-1660, "The Preparation of the Hydrides of Magnesium and Beryllium," by C. E. Holley, Jr., and J. F. Lemons, April 1, 1954.

[3] E. Pietsch, *Z. Elektrochem.*, **39**, 577 (1933).

[4] E. Wiberg and R. Bauer, *Z. Naturforsch.*, **6b**, 171 (1951).