solution rapidly resulted; no solid separated on cooling. Similarly, the lower alcohols appeared to dissolve I with reaction on boiling. Hot sodium hydroxide (2 N) and ammonium hydroxide (concd.) rapidly gave dark brown mixtures with I.

(c) **Reaction with Oxygen.**—Most solutions of I deposited a light tan solid unless carefully protected from oxygen. When air was purposely passed for one hour through a solution of 1.49 g. of I in 25 ml. of n-pentane at room temperature, precipitation of the solid commenced immediately and a thick slurry resulted. The solid was recovered by filtration and washed with benzene. It weighed 0.30 g. Reliable analytical data have not yet been obtained for this compound. It was soluble in water (solution strongly acid) and alcohols and insoluble in organic solvents. It did not melt but darkened at a high temperature. Pentane-soluble products of the oxidation were not examined. Exposure of solid I to the atmosphere results in partial conversion to a pentane-insoluble solid which may be similar to the material described above.

(d) **Reaction with Phenyldichlorophosphine.**—A solution of 6.0 g. (0.0114 mole) of I in 40 g. (0.22 mole) of phenyldichlorophosphine was agitated at 70–80° at 35 mm. for 3 hr. CH_3PCl_2 replaced and volatilized was collected in a trap chilled by a bath of Dry Ice and trichloroethylene.

The trap was found to contain 5.1 g. of pure CH_3PCl_2. This recovery represented 96% of theory. Excess phenyldichlorophosphine was removed by vacuum distillation of the orange reaction product, leaving an oil which readily crystallized. This residue was washed with n-pentane to remove residual phenyldichlorophosphine and then recrystallized from diethyl ether. The recovery of bright yellow product was rather low (57% yield) due to its great solubility in the solvent. It is believed the true yield of $Ni(C_6H_5PCl_2)_4$ was nearly quantitative. The product melted at 91–94°; since the reported value is 86.5°,[5] the solid was recrystallized again. It then melted at 93–94° after sintering at 91–92°. Analysis indicated it to be high purity $Ni(C_6H_5PCl_2)_4$.

Anal. Calcd. for $C_{24}H_{20}Cl_8NiP_4$: Cl, 36.6; Ni, 7.58; P, 16.0. Found: Cl, 36.4; Ni, 7.40; P, 15.9.

Acknowledgment.—The assistance of Donald C. Frokjer and Charles H. Rolston in performing some of the experimental work is acknowledged. Analyses were performed by Dr. Raymond Annino and his associates, of this Laboratory, and by the Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Kinetic Studies of Thiourea Derivatives. II. The Dimethylthioureas[1]

BY WILLIAM H. R. SHAW AND DAVID G. WALKER

unsym-Dimethylthiourea isomerizes in aqueous solutions at elevated temperatures to form dimethylammonium thiocyanate. Experimental first-order rate constants for this reaction under a variety of conditions have been obtained. The isomerization is pH independent over a wide range and no effect of ionic strength was observed. At high pH, however, a complicating parallel reaction takes place. The behavior of *sym*-dimethylthiourea also has been examined. This compound decomposes to form methylamine and methyl isothiocyanate as primary products. Additional reactions by the product species occur. Rate constants and Arrhenius parameters for the isomerization of *unsym*-dimethylthiourea and for the decomposition of the symmetrical derivative are reported. All of the findings are discussed in terms of a possible mechanism.

Introduction

A few papers[2,3] on the chemistry of the dimethylthioureas have recently become available, but no work concerned with the kinetic behavior of these compounds could be found in the literature. Since data on both symmetrical and unsymmetrical dimethylthiourea would be of obvious value in any theoretical interpretation of the relative reactivity of thiourea derivatives, the present[4-7] study was undertaken.

Experimental

Apparatus and Technique.—The apparatus and technique used in the kinetic runs have been described in detail in earlier publications.[5-7]

Analytical Methods.—Ammonium, methylammonium and dimethylammonium ions were separated from the reaction mixture by passing the experimental solution through a cation-exchange column as previously described. Elution was effected by 20 ml. of 0.1 N NaOH, at the usual flow rate. This slight modification was necessary to ensure quantitative elution of the dimethylamine. After elution aliquots

of the neutralized elutriate were used to determine ammonia,[5] methylamine[7] and dimethylamine[8] by spectrophotometric analyses described in detail elsewhere.

The ammonia analysis was not affected by dimethylamine in the concentrations encountered. As previously reported, however, methylamine exerted a moderate interference but suitable corrections could be made.

The methylamine analysis was unaffected by the ammonia and dimethylamine concentrations prevailing in the reaction mixtures. The dimethylamine analysis was similarly uninfluenced by ammonia and methylamine.

Thiocyanate ion was determined spectrophotometrically as before.[6] No significant interference by ammonia, methylamine, dimethylamine or the dimethylthioureas was encountered.

The average deviation of a set of 12 analyses of 0.3 mM dimethylamine was 7.0%. The average deviations for the other analyses have been reported in earlier work.

Compounds.—*sym*-Dimethylthiourea (1,3-dimethyl-2-thiourea) was prepared by the addition of methylamine to methyl isothiocyanate.[9] The product was separated as an oil from water solution twice and then finally crystallized, m.p. 64° (lit.[10] 61°) from benzene which had been partially distilled to remove the last traces of moisture.

Anal. Calcd. for $C_3H_8N_2S$: C, 34.6; H, 7.79; N, 26.9. Found: C, 34.8; H, 7.78; N, 27.0.

unsym-Dimethylthiourea (1,1-dimethyl-2-thiourea) was prepared by the addition of H_2S to dimethylcyanamide.[11]

(1) Presented before the Division of Physical and Inorganic Chemistry, 131st National Meeting of the American Chemical Society held in Miami, Florida, April, 1957.

(2) R. Singh, *J. Indian Chem. Soc.*, **31**, 355 (1954).

(3) R. H. Sahasrabudhey and R. Singh, *ibid.*, **30**, 695 (1953).

(4) Related work from this Laboratory on urea (ref. 5), thiourea (ref. 6) and methylthiourea (ref. 7) has been reported previously.

(5) W. H. R. Shaw and J. J. Bordeaux, THIS JOURNAL, **77**, 4729 (1955).

(6) W. H. R. Shaw and D. G. Walker, *ibid.*, **78**, 5769 (1956).

(7) W. H. R. Shaw and D. G. Walker, *ibid.*, **79**, 2681 (1957).

(8) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," 3rd ed., Vol. IV, D. Van Nostrand Co., Inc., New York, N. Y., 1954, pp. 37–39.

(9) E. C. Horning, Ed., "Organic Syntheses," Coll. Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 617–618.

(10) M. Freund and E. Asbrand, *Ann. Chem. Justus Liebigs*, **285**, 170 (1895).

(11) O. Wallach, *Ber.*, **32**, 1874 (1899).

The product was twice crystallized from water solution, m.p. 158° (lit.[11] 159°).

Anal. Calcd. for $C_3H_8N_2S$: C, 34.6; H, 7.79; N, 26.9. Found: C, 34.5; H, 7.78; N, 26.6.

Results

The rates of formation of four possible reaction products: (1) thiocyanate ion, (2) ammonia, (3) methylamine, and (4) dimethylamine were followed; corresponding empirical first-order rate constants: k_1, k_2, k_3 and k_4 were calculated by the initial rate equation presented before.[7]

The decomposition of *sym*-dimethylthiourea in water solution at elevated temperatures gave methylamine as one reaction product. Carbon oxysulfide also was formed. No thiocyanate, ammonia or dimethylamine could be detected by our rather sensitive analytical techniques. If these products were formed at all, the empirical constants: k_1, k_2 and k_4 characterizing their rate of formation at 100° must be less than: 10^{-10} sec.$^{-1}$, 10^{-9} sec.$^{-1}$ and 10^{-9} sec.$^{-1}$, respectively. Consequently the only rate constants reported for this compound are based on the rate of methylamine formation divided by two. At 100.0 ± 0.1° for reaction times varying from 6.75 to 24.0 hr. the numerical value for k_3 was found to be 2.50 ± 0.16 × 10^{-7} sec.$^{-1}$. This value was obtained with average *sym*-dimethylthiourea concentrations ranging from 19.4 to 992 mM in solutions that were also 0.005 M in H_2SO_4. Thus, in acidic media, the empirical first-order constant, k_3, was found to be independent of average *sym*-dimethylthiourea concentration, $\bar{u}$, and reaction time, t. Consequently the decomposition of this compound can be regarded as a first-order reaction producing methylamine and carbon oxysulfide as ultimate products in acid solution.

In neutral and alkaline media more complex behavior was observed (Fig. 1), and a faint precipitate of mercuric sulfide was detected at pH 9.1 by our usual test. The amount of precipitate increased with increasing pH. These findings are analogous to results reported with methylthiourea.[7] Thus the pH dependence of k_3 in basic solutions can be rationalized by postulating the occurrence of a significant amount of reverse reaction (synthesis of reactant from products); and the formation of sulfide can be explained by assuming the onset of a base-catalyzed parallel reaction (see Discussion).

Runs were also made at different temperatures (Table IA) and in acid media of varying ionic strength. Samples initially 40 mM in *sym*-dimethylthiourea and 12 mM in H_2SO_4 were subjected to a reaction time of 16.8 hr. at 100°. These samples also contained added sodium sulfate ranging in concentration from 0.00 to 0.50 M. No salt effects were encountered.

unsym-Dimethylthiourea was studied in a similar fashion. Two reaction products: thiocyanate and dimethylamine were found in all reaction mixtures. The empirical constants k_1 and k_4 based on these products were independent of $\bar{u}$, t and pH (Fig. 2) over a wide range. These findings are in sharp contrast to results noted above with *sym*-dimethylthiourea. The behavior of k_1, however, is similar

TABLE I

RATE CONSTANTS[a,d] OBTAINED AT VARIOUS TEMPERATURES

Temp., °C. ±0.1	$\bar{u}^a$	t^b	$k_3 \times 10^7$, sec.$^{-1}$
A. *sym*-Dimethylthiourea soln. 0.015 M in HNO_3			
99.6	307	2.93	1.90
100.0	90.8	6.55	2.23
110.0	45.5	6.17	8.10
110.0	93.3	3.07	7.88
120.0	22.7	4.58	28.8
120.0	31.0	2.98	30.1
130.0	9.08	3.62	91.1
130.1	9.33	2.85	108
140.0	9.08	2.78	246
140.0	4.67	2.67	210
B. *unsym.*-Dimethylthiourea soln.			$k_1 \times 10^7$, sec.$^{-1}$
79.5[e]	199.3	12.6	1.44
80.0	99.9	5.83	1.52
90.0[e]	24.9	6.00	5.16
90.0	99.4	6.15	5.68
100.0[e]	24.8	2.90	17.4
100.0	29.4	5.97	20.3
109.5[e]	24.4	2.78	57.2
109.6	9.3	5.85	69.3
119.9	4.35	3.78	230
120.0[e]	9.11	2.40	227

[a] $\bar{u}$ is the average concentration of the dimethylthiourea (mmoles/liter). [b] t is reaction time in hours. [c] The constant k_3 is based on the rate of production of methylamine divided by two. The constant k_1 is based on the rate of production of thiocyanate. [d] For the least squares Arrhenius analysis values representing an average of all data available at 100.0° were substituted for the values at 100° in the above table. [e] These runs were made in 0.015 M HNO_3 solution.

to that of analogous constants obtained with methylthiourea and thiourea. No conversion of thiocyanate to ammonia was observed in the low pH range. This conversion has been noted before; but, because the increased reactivity of *unsym*-dimethylthiourea made a shorter reaction time possible, this reaction was not important in the present work. No methylamine was detected in any of the experimental solutions. At pH 12.6, however, ammonia was observed (k_2 = 38 × 10^{-7} sec.$^{-1}$), the rate of dimethylamine production increased (k_4 = 54 × 10^{-7} sec.$^{-1}$), and a strong positive test for sulfide ion was obtained. Neither ammonia nor sulfide ion was detected in solutions of lower pH. All of these results point, as in previous work, to the onset of a base-catalyzed parallel reaction that produces ammonia and dimethylamine in equimolar amounts.[12] In acid media, neutral solutions, and solutions up to pH 11.4, however, k_1 and k_4 were extremely well behaved constants. At 100 ± 0.1° the numerical values for k_1 and k_4 were: 16.7 ± 1.5 × 10^{-7} sec.$^{-1}$ and 16.9 ± 1.20 × 10^{-7} sec.$^{-1}$, respectively. The fact that k_1 = k_4 within experimental error over this wide range of conditions established the stoichiometry of the reaction rather rigidly. Moreover, a neutral 42.6 mM solution of *unsym*-dimethylthiourea when heated for 90 hours at 127° gave the

(12) This reaction is probably a fairly complex hydrolytic reaction that involves *unsym*-dimethylurea and/or dimethylcyanamide as intermediates. A related reference is cited below.[15]
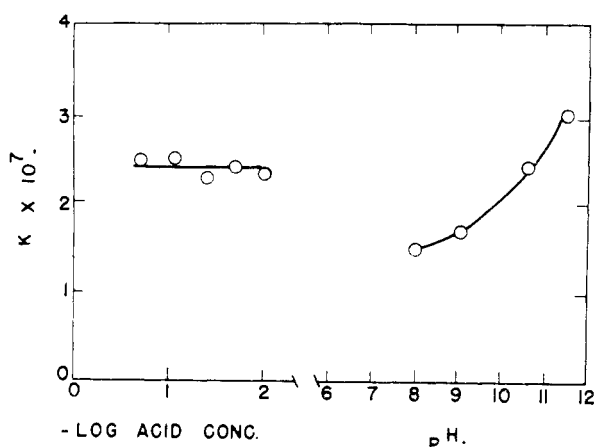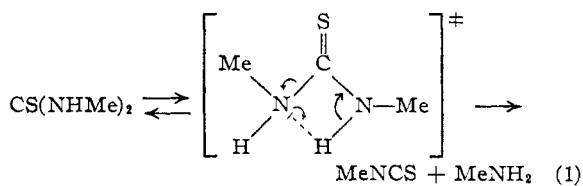
Fig. 1.—Empirical first-order rate constant obtained with *sym*-dimethylthiourea as a function of acid concentration. The constant k_3 is based on the rate of formation of methylamine divided by two. Runs above pH 7 were made in buffered 0.071 M borax solutions. Results recorded below pH 7 were made in H_2SO_4 solutions. All solutions were initially 0.040 M in *sym*-dimethylthiourea. Reaction times were 16.83 hours for the high pH run and 24.0 hours for the low pH run. All measurements were made at 100°.

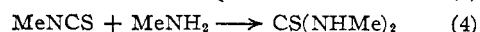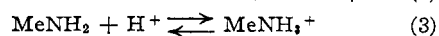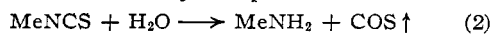following analysis: thiocyanate, 42.3 ± 0.5 mM; dimethylamine, 39 ± 3 mM. Thus, like thiourea, the synthesis of the parent compound from the decomposition products in aqueous media must be very slight. In the absence of solvent, however, equilibrium mixtures of *unsym*-dimethylthiourea and dimethylammonium thiocyanate have been reported[13] to contain 16.9% *unsym*-dimethylthiourea and 80.4% dimethylammonium thiocyanate at 130°. In summary, then, the decomposition of *unsym*-dimethylthiourea is a first-order reaction producing dimethylammonium thiocyanate. The decomposition[14] is not catalyzed by hydrogen or hydroxide ions and is unaffected by ionic strength. Rate constants for this reaction at different temperatures also were obtained (Table I).

Discussion

By analogy to previous work[6] a plausible reaction mechanism for *sym*-dimethylthiourea can be written as

$$CS(NHMe)_2 \rightleftarrows \left[\begin{array}{c} Me \quad\quad S \\ \backslash \quad \parallel \\ \quad C \\ N \quad\quad N—Me \\ / \quad\quad\quad \backslash \\ H \quad\quad\quad H \end{array} \right]^{\ddagger} \longrightarrow$$

MeNCS + MeNH₂   (1)

Additional reactions by the products include

$$MeNCS + H_2O \longrightarrow MeNH_2 + COS\uparrow \quad (2)$$

$$MeNH_2 + H^+ \rightleftarrows MeNH_3{}^+ \quad (3)$$

$$MeNCS + MeNH_2 \longrightarrow CS(NHMe)_2 \quad (4)$$

In acid solution the experimental rate constant, k_3, is presumably the result of reaction 1 followed quickly by reactions 2 and 3. Reaction 4 does not occur, being suppressed by the rapid occurrence

(13) H. Salkowski, *Ber.*, **26**, 2497 (1893).

(14) The hydrolytic reaction[13,15] is, however, base catalyzed.
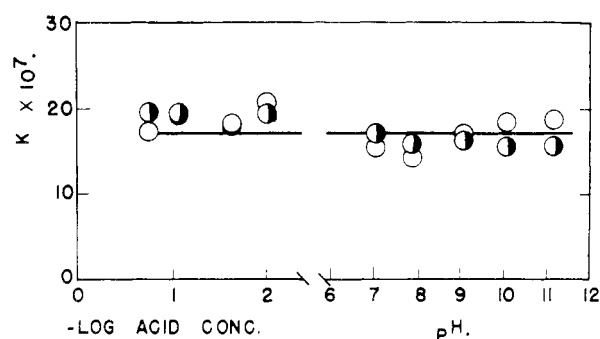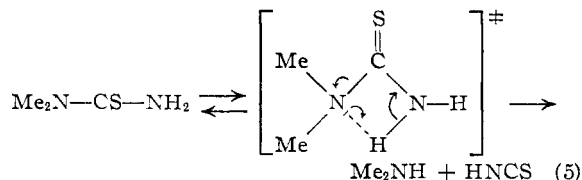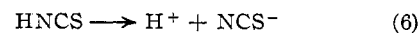

Fig. 2.—Empirical first-order rate constants obtained with *unsym*-dimethylthiourea as a function of acid concentration. The constants k_1 (O) and k_4 (◑) are based on the rate of formation of thiocyanate and dimethylamine, respectively. Runs above pH 7 were made in buffered 0.008 M borax solutions. Results recorded below pH 7 were made in HNO_3 solutions. An initial concentration of 42.7 mM *unsym*-dimethylthiourea was used with reaction times of 5.47 hours on the acid side and 4.17 hours on the high pH side. All data were collected at 100°.

of reactions 2 and 3. In neutral and basic solutions, however, reaction 4 does take place. In alkaline media, a parallel base-catalyzed reaction, producing H_2S and an unstable fragment[15] which further decomposes to yield methylamine, is also present.

A similar mechanism for *unsym*-dimethylthiourea would predict two primary reaction products produced in equimolar amounts

$$Me_2N—CS—NH_2 \rightleftarrows \left[\begin{array}{c} Me \quad\quad S \\ \backslash \quad \parallel \\ \quad C \\ N \quad\quad N—H \\ / \quad\quad\quad \backslash \\ Me \quad\quad\quad H \end{array} \right]^{\ddagger} \longrightarrow$$

Me₂NH + HNCS   (5)

Also

$$HNCS \longrightarrow H^+ + NCS^- \quad (6)$$

$$Me_2NH + H^+ \rightleftarrows Me_2NH_2{}^+ \quad (7)$$

No significant synthesis (reverse of reaction 5) is possible in aqueous media since HNCS is a strong acid. The rate constants (Fig. 2) are, consequently, pH independent.

The absence of methylamine in *unsym*-dimethylthiourea reaction mixtures and the lack of dimethylamine in *sym*-dimethylthiourea reaction solutions is strong experimental proof that the methyl groups do not migrate during reaction. Thus all products can be predicted by assuming intramolecular hydrogen transfer and dissociation of the activated complex as indicated (reactions 1 and 5).

Over the temperature range studied, the rate constants for the decompositions of the dimethylthioureas follow the simple Arrhenius relationship. A least squares analysis of the data presented in Table I gave the following Arrhenius parameters[16]

(15) Perhaps a carbodiimide is formed which undergoes further reaction with the solvent. See for example: H. G. Khorana, *Chem. Revs.*, **53**, 145 (1953).

(16) These parameters will reproduce the rate constants in Table IA with an average deviation of 9%.

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.

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

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.

Fluoroarsenites

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

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: $F_4Sb\diagup^F_{\diagdown F}\diagdown AsF_2$.

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

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

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

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

(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).