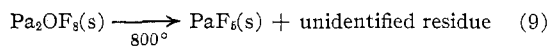


The oxyfluoride is hygroscopic, slightly soluble in water, and very soluble in hydrofluoric acid solutions. It is volatile under vacuum above 500° and partly decomposes at 800° and higher temperatures, yielding PaF<sub>5</sub> and other unidentified products (eq. 9). Thus, by



successive reactions 7, 8, and 9, it is possible to prepare anhydrous PaF<sub>5</sub> from Pa<sub>2</sub>O<sub>5</sub> without the use of vigorous fluorinating agents.

**Acknowledgment.**—The author is indebted to Dr. S. Siegel and Mrs. E. Gebert Sherry for the X-ray analyses and to Mr. D. J. Henderson for the  $\alpha$  pulse analyses. He also wishes to express his thanks to Dr. K. W. Bagnall of the Atomic Energy Research Establishment, Harwell, England, for providing initial samples of Pa<sup>231</sup> and the inducement to undertake the present line of research. The work was begun during a visit to Harwell in 1959 and was later completed at Argonne.

CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM & HAAS COMPANY:  
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## The Arsenic Trifluoride–Arsenic Trichloride System

BY JOHN K. RUFF AND GROVER PAULETT

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The species AsF<sub>2</sub>Cl and AsFCl<sub>2</sub> have been observed in mixtures of AsCl<sub>3</sub> and AsF<sub>3</sub> by two independent methods. The formation constants of AsF<sub>2</sub>Cl and AsFCl<sub>2</sub> have also been determined.

Exchange processes have been observed in phosphorus trihalide systems<sup>1–3</sup> and several mixed phosphorus trihalides have been characterized.<sup>4,5</sup> No examples, however, of mixed arsenic trihalides have been completely characterized, although evidence for such species was found in a study of a mixture of AsCl<sub>3</sub> and AsBr<sub>3</sub>.<sup>3</sup> The Raman spectra of these mixtures contained bands not found in the spectra of the components. These bands were attributed to the exchanged products AsCl<sub>2</sub>Br and AsClBr<sub>2</sub>. Raman spectroscopy, on the other hand, gave no evidence for the existence of AsF<sub>2</sub>Cl and AsFCl<sub>2</sub><sup>3</sup> in mixtures of arsenic trifluoride and arsenic trichloride. Attempts to prepare these species by partial fluorination of AsCl<sub>3</sub> have not been successful either.<sup>6</sup> However, their existence in mixtures of AsF<sub>3</sub> and AsCl<sub>3</sub> was demonstrated by using F<sup>19</sup> n.m.r. and mass spectrometry.

### Experimental

**Materials.**—The arsenic trifluoride and arsenic trichloride used were obtained from commercial sources. Each was purified by distillation in an inert atmosphere. The former was distilled from sodium fluoride. Pyridine (Karl Fischer reagent grade) was used without further purification.

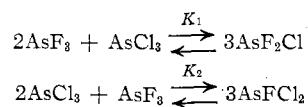
**N.m.r. Study.**—The F<sup>19</sup> n.m.r. spectra were obtained with a Varian Model 4300B spectrometer operating at 40 Mc. Chemical shifts were determined with CCl<sub>3</sub>F as an internal standard by the side-band technique. The relative areas of the three peaks were obtained by use of an integrating circuit. All solutions were prepared by weight in a nitrogen-filled drybox.

**Mass Spectral Study.**—The mass cracking patterns were obtained with a Consolidated Systems Corporation high speed

mass spectrometer utilizing an ionizing voltage of 70 volts. The gaseous mixtures were prepared in 1–3-ml. calibrated bulb, equipped with Teflon needle valves in the following manners. One bulb was filled with a measured pressure of AsCl<sub>3</sub> (approximately 10 mm.). This was condensed into a slightly larger bulb with liquid nitrogen. Then the first bulb was filled to the desired pressure with AsF<sub>3</sub>. The AsF<sub>3</sub> was then condensed into the bulb containing the AsCl<sub>3</sub>. The sample bulb was warmed and allowed to age approximately 0.5 hr. Several samples were prepared by allowing known amounts of the gaseous components to mix by diffusion in a closed, greaseless system. No differences in the values for  $K_1'$  and  $K_2'$  were found between samples prepared by the two methods. The mass cracking pattern of the mixture was obtained by expanding the sample directly into the inlet system (approximately 2 l. in volume). The sensitivities of AsCl<sub>3</sub> and AsF<sub>3</sub> were also obtained by this method. The pressure in the inlet system was determined by means of a thermocouple gage.

### Mass Spectral Studies

The mass spectrum of a vapor-phase mixture of AsCl<sub>3</sub> and AsF<sub>3</sub> contains parent molecule ions for the exchanged species AsF<sub>2</sub>Cl and AsFCl<sub>2</sub>. The assignment of these peaks to the exchanged species was made on the basis of their having the correct  $m/e$  ratio and the correct isotopic peaks for chlorine. The fragment ion AsFCl<sup>+</sup> at  $m/e$  129 was also obtained from the exchanged species. All other fragment peaks will be obtained both from exchanged and unexchanged species. Only mixtures which contained excess AsF<sub>3</sub> were used due to the relatively low volatility of AsCl<sub>3</sub>. The mass spectra of a series of mixtures of AsF<sub>3</sub> and AsCl<sub>3</sub> were obtained to evaluate the two equilibrium constants necessary to describe the system. The equilibrium constants are defined for the equilibria



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TABLE I  
 MASS SPECTRAL ANALYSIS OF  $\text{AsCl}_3$ - $\text{AsF}_3$  MIXTURES

AsF <sub>3</sub> : AsCl <sub>3</sub>	Peak heights of the parent ions AsX <sub>3</sub> <sup>+</sup> (arbitrary units)				K <sub>1</sub> ' × 10 <sup>3</sup>	K <sub>2</sub> ' × 10 <sup>3</sup>
	AsF <sub>3</sub>	AsCl <sub>3</sub>	AsF <sub>2</sub> Cl	AsFCl <sub>2</sub>		
1.37	39.6	24.0	7.3	5.0	10	5.5
3.78	93.0	18.4	11.0	5.8	8.4	6.2
3.52	136	27.6	16.5	8.3	8.8	5.5
5.97	69.5	8.2	6.7	3.0	7.6	5.8
7.68	103	9.7	8.8	3.9	6.6	6.1
4.01	125	23.1	14.0	7.2	7.6	5.6
3.08	107	27.6	14.4	8.0	9.4	6.3
3.52	52.7	11.3	6.3	3.5	8.0	6.4
4.21	81.7	14.4	8.5	4.7	6.4	6.1
					8.1 ± 0.9	5.9 ± 0.3

where

$$K_1 = [\text{AsF}_2\text{Cl}]^3 / [\text{AsF}_3]^2 [\text{AsCl}_3]$$

and

$$K_2 = [\text{AsFCl}_2]^3 / [\text{AsCl}_3]^2 [\text{AsF}_3]$$

The pressure of each species in the system is proportional to the peak height,  $P$ , for the parent molecular ion divided by the sensitivity,  $S$ , of the detecting system to that particular ion. The equilibrium constant may be written in terms of the peak height as

$$K_1 = \frac{P_{\text{AsF}_2\text{Cl}}^3}{P_{\text{AsF}_3}^2 P_{\text{AsCl}_3}} \frac{S_{\text{AsF}_3}^2 S_{\text{AsCl}_3}}{S_{\text{AsF}_2\text{Cl}}^3}$$

A similar expression may be written for  $K_2$ . An apparent equilibrium constant may be obtained from the peak heights which is related to the equilibrium constant by  $K_1 = K_1' f$  where  $f$  is the ratio of sensitivities. The value of  $f$  should be approximately 1 as the sensitivities for the parent ions of  $\text{AsFCl}_2$  and  $\text{AsF}_2\text{Cl}$ , which could not be obtained, should be close to the sensitivities for  $\text{AsF}_3$  and  $\text{AsCl}_3$ . In addition to the error introduced by not knowing the sensitivities for  $\text{AsFCl}_2$  and  $\text{AsF}_2\text{Cl}$ , another large error is in reading the small peak heights obtained for the exchanged species. The values calculated for  $K_1'$  and  $K_2'$  are listed in Table I.

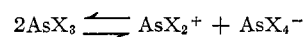
Equilibrium was established rapidly and no difference was observed in the values of  $K_1'$  and  $K_2'$  obtained on aged and freshly prepared mixtures. In fact, equilibrium was apparently established before it was possible to obtain the mass spectrum. Extensive absorption of the arsenic trihalides on the walls and/or in the grease in the inlet system did not appear to be a serious problem either. The ratios of  $\text{AsF}_3$  to  $\text{AsCl}_3$  determined by mass spectroscopy agreed reasonably well with the stoichiometric ratios. After the sample had been expanded into the inlet system and allowed to age for approximately 30 min. a decrease in pressure was observed which may indicate slow absorption of the arsenic trihalides.

### N.m.r. Study

The  $\text{F}^{19}$  n.m.r. spectrum of a mixture of  $\text{AsCl}_3$  and  $\text{AsF}_3$  contains three bands: A,  $40.4 \pm 0.2$  p.p.m.; B,  $49.0 \pm 0.2$  p.p.m.; and C,  $67.4 \pm 0.1$  p.p.m. (*vs.*  $\text{CCl}_3\text{F}$ ). Band A is the largest band in the spectrum even at high ratios of  $\text{AsCl}_3$  to  $\text{AsF}_3$ . However as this ratio is increased band A decreases in size relative

to the other two bands while band C appears to increase in size relative to band B, especially at  $\text{AsCl}_3/\text{AsF}_3$  ratios of 5 or higher. This suggests that of the three fluorine-containing species being observed by n.m.r., band A is due to a species containing the most fluorine atoms per arsenic atom while band C is due to a species that contains the least. The relative chemical shifts of these three bands also tend to support this thesis since replacement of fluorine by chlorine in either nitrogen trifluoride or phosphorus trifluoride results in a progressive shift in the observed  $\text{F}^{19}$  n.m.r. band of the substituted species to higher field:  $\text{NF}_3$  ( $-145$  p.p.m.),  $\text{NF}_2\text{Cl}$  ( $-141$  p.p.m.), and  $\text{NFC}_2\text{Cl}$  ( $-129$  p.p.m.)<sup>7</sup>; and for the series  $\text{PF}_3$  ( $+35.1$  p.p.m.),  $\text{PF}_2\text{Cl}$  ( $+35.6$  p.p.m.), and  $\text{PFCl}_2$  ( $+57.8$  p.p.m.)<sup>8</sup> *vs.*  $\text{CCl}_3\text{F}$ .

Band A in the mixture is believed to be due to ion-exchanged  $\text{AsF}_3$ , since the  $\text{F}^{19}$  n.m.r. band for pure  $\text{AsF}_3$  is observed at 41.3 p.p.m. The assignment of the other two bands is more difficult because a number of species may exist in the mixture. The self-ionization process



has been proposed for the pure arsenic trihalides,  $\text{AsCl}_3$  and  $\text{AsF}_3$ ,<sup>9,10</sup> and it is likely that when these trihalides are mixed a number of ions containing both fluorine and chlorine are also produced (*e.g.*,  $\text{AsFCl}_2^+$ ,  $\text{AsFCl}_3^-$ , etc.) in addition to the two possible covalent arsenic chlorofluorides. However no data are available concerning the conductivity of these mixtures, so that the relative importance of ionic species cannot be assessed and thus a conclusive assignment of bands B and C cannot be made. The assignment felt to be most compatible with the available data is that band B is due to the species  $\text{AsF}_2\text{Cl}$  and band C is due to  $\text{AsFCl}_2$ .

Determination of the relative areas of the three bands in a series of mixtures of  $\text{AsCl}_3$  and  $\text{AsF}_3$  allowed the calculation of the equilibrium constants  $K_1$  and  $K_2$  as previously defined. These values are listed in Table II. The reproducibility of the values obtained was not good, especially when solutions containing low ratios of  $\text{AsCl}_3$  to  $\text{AsF}_3$  were used. This is believed

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TABLE II  
 N.M.R. ANALYSIS OF  $\text{AsCl}_3$ - $\text{AsF}_3$  MIXTURES

AsCl <sub>3</sub> : AsF <sub>3</sub>	Moles of AsX <sub>3</sub> × 10 <sup>2</sup>					
	AsF <sub>3</sub>	AsCl <sub>3</sub>	AsF <sub>2</sub> Cl	AsFCl <sub>2</sub>	K <sub>1</sub> × 10 <sup>2</sup>	K <sub>2</sub> × 10 <sup>2</sup>
4.30	2.43	13.0	0.67	1.09	3.9	3.2
6.49	2.87	24.7	0.86	1.81	3.1	3.4
7.57	1.69	18.9	0.77	1.33	8.5	3.9
7.73	2.15	24.4	0.86	1.71	5.6	3.9
10.07	2.07	33.2	0.85	2.48	4.3	6.7
11.68	1.91	37.0	0.82	2.58	4.1	6.6
					4.9 ± 1.2	4.6 ± 1.4

to be due to some overlapping of bands A and B, when band A was much larger in size than band B. Better constancy of the data was found, however, when the areas of the bands were similar in size. This necessitated the use of solutions containing high  $\text{AsCl}_3$  to  $\text{AsF}_3$  ratios and limited the range which could be studied.

Addition of excess acetonitrile to several mixtures of  $\text{AsCl}_3$  and  $\text{AsF}_3$  results in an average shift to higher field of bands A, B, and C by 6.9, 4.9, and 2.2 p.p.m., respectively. Although quantitative data are lacking, no pronounced change in the relative areas of the  $\text{F}^{19}$  n.m.r. bands occurred upon the addition of acetonitrile. However, when pyridine, NaF, or NaCl was added to these acetonitrile solutions, the two small bands (B and C) disappeared. The same phenomenon occurred when either an excess or deficiency of pyridine was added to several of the neat mixtures. The band (A) attributed to  $\text{AsF}_3$  was shifted upfield by 2.5 p.p.m. upon the addition of less than 5 mole % of pyridine to a 1:1 mixture of  $\text{AsCl}_3$  and  $\text{AsF}_3$ . The area of this band after the addition was relatively unchanged. On the other hand, addition of NaF or NaCl to the neat mixtures resulted only in broadening of the bands.

Two samples of the neat mixtures with  $\text{AsCl}_3$  to  $\text{AsF}_3$  ratios of 4:1 and 2:1 were heated to 75°. Essentially no change in the  $\text{F}^{19}$  n.m.r. spectra of these mixtures occurred during heating except for a broadening of all three of the peaks. In order to determine whether the broadening was due to an increase in the rate of exchange, a sample of carefully purified arsenic trifluoride was heated to 75° and the band width at half-amplitude was determined as a function of temperature. Little or no difference was found between the broadening of the  $\text{AsF}_3$  peak in the mixtures and in the pure sample. The broadening of the band in the pure  $\text{AsF}_3$  sample could be due to the quadrupole moment of arsenic, an increase in rate and/or extent of the self-ionization process, or both. The same effects could be responsible for the observed broadening of the three bands in the mixed arsenic trihalides. Unfortunately, it is impossible to determine what the temperature effect, if any, on the rate of the fluorine-chlorine exchange was.<sup>11</sup>

### Discussion

The low value of the formation constants,  $K_1$  and

$K_2$ , for the exchanged species  $\text{AsF}_2\text{Cl}$  and  $\text{AsFCl}_2$  probably explains why no evidence for these species was obtained in the Raman spectral study and why partial fluorination of  $\text{AsCl}_3$  apparently produced only  $\text{AsF}_3$ . The low degree of interaction between the two halides is again reflected by their immiscibility below 19°. If a statistical redistribution of chlorine and fluorine on the arsenic had occurred on mixing, the free energy of the exchange reaction would be zero. The free energy of the exchange reactions may be estimated from the expression<sup>1</sup>

$$\Delta F = \frac{-RT}{3} \ln \left( \frac{K}{27} \right)$$

where  $K$  is either  $K_1$  or  $K_2$ . The values of  $\Delta F$  thus obtained for  $\text{AsF}_2\text{Cl}$  and  $\text{AsFCl}_2$  are in the range of 1.4 to 1.5 kcal./mole. The values of  $\Delta F$  obtained for this system are in marked contrast with those found in the systems  $\text{As}[\text{N}(\text{CH}_3)_2]_3$ - $\text{AsF}_3$  and  $\text{As}(\text{OCH}_3)_3$ - $\text{AsF}_3$ .<sup>12</sup> For example, the free energy of formation of  $\text{AsF}_2\text{N}(\text{CH}_3)_2$  was estimated to be about -7 kcal./mole and in fact dimethylaminodifluoroarsine may be distilled without decomposition. All the other exchanged species in these two systems were found to have negative values of  $\Delta F$ . The reason for the great difference in stability of  $\text{AsF}_2\text{Cl}$  and  $\text{AsF}_2\text{N}(\text{CH}_3)_2$  is not clear.

The similarity in the magnitude of  $K_1$  and  $K_2$  obtained from the mass spectral study of the vapor-phase mixtures and the n.m.r. study of the liquid-phase mixtures might not have been expected. Since nothing is known of the mechanism of exchange or the thermodynamic properties of the exchanged species, little comment can be made. However, it is perhaps not warranted to assume that the n.m.r. assignments are correct, since these values correspond reasonably well. Further work will be necessary before a fuller understanding of this system is achieved.

The disappearance of the bands attributed to the two exchanged species upon addition of base (*e.g.*, pyridine or sodium fluoride) is felt to be due to an increase in the rate of exchange. Another alternative is either the partial or complete removal of one or more of the trihalide species from the exchange equilibria by complex formation. Complexation of the arsenic trihalide species is perhaps evidenced by the shift of the  $\text{F}^{19}$  n.m.r. bands to higher field upon addition of excess acetonitrile to the mixtures. A similar shift to higher field of the  $\text{AsF}_3$  band is also noted when pyridine is added to the neat mixtures, to a solution of  $\text{AsCl}_3$  and

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AsF<sub>3</sub> in acetonitrile, or to pure AsF<sub>3</sub>. The observed increased shielding of the fluorine nucleus is to be expected if complexing occurred. However, a small shift to higher field would also occur if the rate of exchange in the mixture was increased to the extent that the three bands coalesced.

In an equimolar mixture of AsF<sub>3</sub> and AsCl<sub>3</sub> containing an equivalent amount of base, the disappearance of the two small bands B and C could be due to complex formation. Even if the base is present in slightly less than an equivalent amount, reduction in the amount of one of the free symmetrical trihalides through complex formation could have occurred to such an extent that the concentration of the exchanged species was below the level of detection. However, in a mixture containing AsCl<sub>3</sub>, AsF<sub>3</sub>, and pyridine in a

10:10:1 mole ratio, substantial amounts of the free trihalides will still be present even if complex formation does occur.<sup>13</sup> Therefore observable amounts of the exchanged products would be expected in this mixture. Since the small bands (B and C) were not observed, it is concluded that, at least in this case, the addition of pyridine resulted in an increase in the rate of exchange.

**Acknowledgments.**—The authors wish to thank Dr. F. A. Johnson for some of the F<sup>19</sup> n.m.r. calculations. This work was performed under Contract No. DA-01-021 ORD-11878 (Z) Mod. No. 7.

(13) The implicit assumption made is that a complex of the constitution pyridine:10AsX<sub>3</sub> is not stable in the mixture. Exchanged species would be detected even if the complex pyridine:9AsF<sub>3</sub> was inert.

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## The Hydrothermal Synthesis of Sodium Amphiboles

By T. E. GIER, N. L. COX, AND H. S. YOUNG

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Sodium magnesium silicates with the amphibole structure have been obtained as fine, exceptionally flexible fibers up to 4 in. long from a Na<sup>+</sup>-Mg<sup>+2</sup>-SiO<sub>3</sub><sup>-2</sup> system under hydrothermal conditions. Co<sup>+2</sup> and Ni<sup>+2</sup> substitute entirely or partially for magnesium in the structure to give pink and green fibers, respectively.

### Introduction

The term amphibole describes a large class of naturally occurring metal silicates whose distinctive feature is a double chain of (SiO<sub>4</sub>) tetrahedra as the fundamental element of the crystal structure. A number of X-ray structure determinations of amphiboles have been made,<sup>1-5</sup> and the silicate chains have been shown to be held together face to face in the crystal by octahedrally coordinated cations and edge to edge by cations in hexahedral (pseudo-cubic) coordination. The crystal structure of the amphiboles is susceptible in nature to extensive substitution at different sites by a variety of cations present in the original magma or during subsequent metamorphism. As a result, probably over 100 amphiboles have been described, each differing slightly in stoichiometry. The mineralogical literature contains many references to the composition<sup>6-8</sup> and synthesis<sup>9-14</sup> of representative members

of this class of silicates. This paper is concerned with (1) the hydrothermal synthesis of sodium magnesium amphiboles and fluoro amphiboles as fine, extremely flexible fibers from simple aqueous systems containing Na<sup>+</sup>, Mg<sup>+2</sup>, SiO<sub>3</sub><sup>-2</sup> (or polymers thereof), and F<sup>-</sup>; and (2) fine, fibrous sodio-amphiboles in which the magnesium is replaced partially or entirely by Co<sup>+2</sup> or Ni<sup>+2</sup>.

### Experimental

**Materials.**—Reactants were analytical reagent grade chemicals from conventional sources. Colloidal SiO<sub>2</sub> was base-stabilized "Ludox"<sup>15</sup> LS (15% SiO<sub>2</sub>) or SM (30% SiO<sub>2</sub>). All solutions were prepared with distilled water.

**Apparatus and Procedures. Syntheses.**—The syntheses were carried out in collapsible capsules fabricated from 0.375-1.0 in. diameter platinum tubing having a wall thickness of 0.005 in. with crimped and welded end closures. The capsules were charged with the reagent solutions (usually 1-2 M) in the desired ratios, leaving 30-50% of the capsule volume empty prior to final sealing. This free volume prevented rupture of the capsules during heating. The capsules were then placed in a heavy-walled pressure vessel, pressured to about 1000 atm. with argon

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(15) Industrial and Biochemicals Dept., E. I. du Pont de Nemours and Company.