606. *The Fluorination of Some Volatile Chlorides with Ammonium Fluoride.*

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Halogen exchange occurs when ammonium fluoride is heated with certain volatile chlorides. In some cases useful yields of monofluoride chlorides may be obtained without special control of the conditions.

SEVERAL applications of ammonium fluoride for the fluorination of covalent halides have been reported, but their nature suggests that a more complete survey of its potentialities in this field is required. It is, for example, one of the few reagents suitable for halogen-exchange fluorination of arsenic halides under mild conditions (MacIvor, *Chem. News*, 1874, **30**, 169; 1875, **32**, 258; Long, Emeléus, and Briscoe, *J.*, 1946, 1123). Moreover, the ammonium fluoride–ammonium chloride couple stands high in a table recently drawn up by Woyski (*J. Amer. Chem. Soc.*, 1950, **72**, 919) in which fluoride–chloride couples are listed in order of increasing free energies of fluoride–chloride exchange processes, so that equilibrium conditions can be expected to be favourable to occurrence of halogen exchange between ammonium fluoride and most covalent chlorides.

In the present experiments halogen exchange was observed between ammonium fluoride and chlorides of silicon, phosphorus, arsenic, and antimony, and of the halides examined *NN*-dichloroethylamine alone failed to react. From a practical viewpoint the reactions with chlorides of silicon and phosphorus which were examined are notable for the ease with which the monofluoride chlorides listed below may be obtained even without recourse to any special control of reaction conditions :

Chloride	$SiCl_4$	$SiEt_2Cl_2$	PCl_3	$POCl_3$
Fluoride chlorides isolated	$SiCl_3F$	$SiEt_2ClF$	PCl_2F	$POCl_2F$ $POClF_2$

Except for diethylchlorofluorosilane, not previously described, such products have been obtained by Booth and his co-workers (*J. Amer. Chem. Soc.*, 1932—49) by the use of antimony trifluoride only under rather elaborately controlled conditions. A similar predominance of monofluorinated intermediates has been observed in these fluorinations with antimony trifluoride, and has been ascribed by Booth and Bozarth (*ibid.*, 1939, **61**, 2927) to the progressively more rapid fluorination of the successive intermediates under the same experimental conditions.

Fluorination of arsenic trichloride failed to yield the fluoride chlorides, which are as yet unknown. In similar experiments with methyldichlorostibine and dimethylchlorostibine the sole volatile product was trimethylstibine, obtained in almost quantitative yield, suggesting complete disproportionation of the methylfluorostibines.

EXPERIMENTAL.

The chlorides were heated under reflux with dry, finely crystalline, AnalaR-quality ammonium fluoride, and the gaseous or more volatile fluorinated material passing through the condenser was retained in a cold trap. The ammonium fluoride used was found by analysis to contain not more than 2% of the hydrogen fluoride. The product from the cold trap was fractionally distilled through an 18″ column packed with glass helices and having a water-cooled or low-temperature head, as appropriate. Where refluxing temperatures were low, reactions became very slow after an initial period of more rapid fluorination but such reactions required little attention. Similar proportions of the various products were obtained from the initial and later stages of these reactions. Low-boiling fluorides were purified and identified tensimetrically in a vacuum system.

Fluorination of Silicon Tetrachloride, Phosphorus Trichloride, and Phosphoryl Trichloride.—Experimental data are summarised in the table.

Reactants (g.)	Reaction time (hrs.)	Product	Yields (g.)	B. p./mm.	Cl, %	
					Found	Calc.
$SiCl_4$, 170 ...... NH_4F, 75	100	$SiCl_3F$	5	12·0–12·4°/758	—	—
		SiF_4	8	—	—	—
PCl_3, 200 .... NH_4F, 68	100	PCl_2F	3·5	13·4—13·9°/757	58·1	58·7
		PF_3	9	—	—	—
$POCl_3$, 154 ...... NH_4F, 74	8	$POCl_2F$	16	52·0—52·2°/745	51·5	51·8
		$POClF_2$	7	2·5—2·9°/745	28·5	29·6
		POF_3	39	—	—	—

Boiling points and vapour pressure curves of the fluoride chlorides agreed closely with those reported by Booth (*loc. cit.*). For chloride analyses the compounds were redistilled, weighed, and absorbed in alkali, with standard vacuum technique, and the chloride was determined gravimetrically.

Fluorination of Diethyldichlorosilane.—The reaction was carried out in a flask fitted with fractionating column, and bearing a side-arm through which successive small quantities of ammonium fluoride could be introduced as reaction proceeded. In a typical fluorination 0·35 g.-mol. of diethyldichlorosilane (b. p. 128—130°) was carefully heated with ammonium fluoride (4 g.) and the reflux ratio adjusted so as to keep the distillation temperature at 95—105°. As the reaction slackened a further small quantity (2—3 g.) of ammonium fluoride was added through the side-arm, and the process repeated until a total of 0·65 g.-mol. of ammonium fluoride had been added. Addition of xylene towards the end of the operation rendered distillation of fluorinated material more complete, and also served to keep the reaction mixture mobile. Redistillation of the product gave about 30 g. of diethyldifluorosilane, b. p. 62·0—62·5°/760 mm., and 4 g. of *diethylchlorofluorosilane*, b. p. 96—97°/758 mm. For analysis the compounds were absorbed in excess of 0·7N.-alkali, the solutions were boiled to ensure complete hydrolysis, and excess of alkali was back-titrated. The chlorine content of the fluoride chloride was determined gravimetrically and by Mohr's titration method [Found : (*a*) Fraction, b. p. 62·0—62·5° : 0·0158 equiv. of acid/g. Calc. for $C_4H_{10}F_2Si$: 0·0161. (*b*) Fraction, b. p. 96—97° : 0·0140 equiv. of acid/g. ; Cl, 26·0. $C_4H_{10}ClFSi$ requires 0·0142 equiv./g. ; Cl, 25·3%].

Fluorination of Arsenic Trichloride.—This was carried out by a procedure similar to that for the fluorination of diethyldichlorosilane. The only product was arsenic trifluoride, b. p. 60—61°, with no indication of the presence of material of intermediate volatility.

Reactions of Ammonium Fluoride with Methyldichlorostibine and Dimethylchlorostibine.—These reactions were carried out under nitrogen to avoid complications from oxidation. Both stibines reacted readily at 90°. Volatile products from both reactions were found from measurement of vapour pressures and vapour densities to consist of trimethylstibine only. As a typical yield, 342 c.c. were obtained from 4·5 g. of dimethylchlorostibine (Found : *M*, 167·3. Calc. for C_3H_9Sb : *M*, 166·8).

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