by either their use of a different graphite, or a differently treated graphite, or a different calorimeter temperature, since the effect caused by all these was tested in the present experiments and found to produce only minor variations. They did not describe their calorimeter in detail, but from their description it is evident that their calorimeter was not adequately isolated from its surroundings and that their calibration heater was isolated from their calorimeter to some extent. It is apparent that their thermocouple, therefore, was not located in the same position relative to the heat flow during calibration and during reaction. The location was such that a high final result would be expected.

The results reported here were derived from a series of experiments performed in calorimeters which were successively refined to eliminate variable heat losses, and the heat losses were then measured or (in the case of small ones) estimated. Experiments were performed with a variety of graphite samples some of which were outgassed at 1000° in high vacuum. All the results obtained were in the range 72–90 cal./g. carbon. From the most refined experiments the value 81 cal./g. was chosen as best representing the value for Acheson graphite, and the value seems to vary from sample to sample in the manner previously described.

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[CONTRIBUTION FROM THE UNIVERSITY OF ILLINOIS AND WESTERN RESERVE UNIVERSITY]

Synthesis and Fluorination of Phosphorus(III) β-Chloroethoxy Dichloride[1]

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Phosphorus(III) β-chloroethoxy dichloride has been synthesized by a new procedure in which ethylene chlorohydrin is allowed to react with phosphorus(III) chloride. Phosphorus(III) β-chloroethoxy dichloride has been fluorinated by means of the Swarts reaction to give phosphorus(III) β-chloroethoxy difluoride. The above compounds have been purified and characterized by the determination of their molecular weights, percentage compositions, freezing points, vapor pressures, boiling points, heats of vaporization, Trouton's constants and liquid densities. The solubilities of the above compounds in seven solvents have been noted. Certain chemical properties, including hydrolytic reactions and the corrosion of steel, have been observed.

This investigation is a continuation of a study of the effects of the substitution of an alkoxy radical for a halogen atom in phosphorus(III)[4] and boron[5] halides. In this study, it was of particular interest to observe the effect of the Swarts reaction on the chlorine atoms in phosphorus(III) β-chloroethoxy dichloride.

Experimental

Preparation and Purification of Phosphorus(III) β-Chloroethoxy Dichloride.—Kabachnik and Rossiĭskaya[6] have prepared phosphorus(III) β-chloroethoxy dichloride by allowing ethylene oxide to react with phosphorus(III) chloride. In this investigation phosphorus(III) β-chloroethoxydichloride was prepared by a new procedure which is a modification of the method of Menschutkin.[7] One mole of purified anhydrous ethylene chlorohydrin was added dropwise to one mole of phosphorus(III) chloride with vigorous stirring at a reaction temperature of 0°. The ethylene chlorohydrin was added at a rate of about 80 g. per hour. The reactor was a three-necked flask fitted with a glass stirrer with a mercury seal, a water-cooled condenser which was attached to a drying tube containing barium oxide, and a dropping funnel. Agitation was continued while the reaction mixture was allowed to warm slowly to room temperature to facilitate the evolution of hydrogen chloride. The remaining mixture of reaction products was distilled under a pressure of 40 mm. The residual liquid in the still pot at about 100° was regarded as impure phosphorus(III) β-chloroethoxy dichloride (yield about 77% based on ethylene chlorohydrin). The product was distilled under a pressure which varied from 5–10 mm. in a fractionating column packed with glass helices.[8] The vapor of the purified product condensed at 70° (5 mm.) and 75° (10 mm.) as a colorless liquid (yield of about 72%).

Fluorination of Phosphorus(III) β-Chloroethoxy Dichloride.—The method and apparatus used for the fluorination by the Swarts reaction were the same as described earlier,[4] except no catalyst was required. The fluorination was begun at room temperature, but during the course of the reaction the generator became warm, attaining a maximum temperature of 60°. The pressure within the generator was approximately 50 mm.

The products of fluorination were fractionally distilled in a modified Dufton column.[9] The column was operated at approximately atmospheric pressure until the fractions with very low boiling points were removed. The desired product distilled at about 14° *ca.* 40 mm.

Analyses.—The samples were collected and weighed in glass ampoules of approximately one-milliliter capacity. These samples were hydrolyzed in a slight excess of dilute (*ca.* 0.5 *N*) solution of sodium hydroxide. The concentration of caustic was maintained as low as possible as a precaution against obtaining silica in the solution, which would interfere with the analysis for phosphorus.

Chlorine was determined by the Volhard procedure, the necessary precautions being exercised to prevent the phosphite ion from reducing the silver ion.[10] Phosphorus was determined gravimetrically as magnesium pyrophosphate after oxidation of the phosphite ion to the phosphate ion with bromine and nitric acid.[4] Carbon and hydrogen were determined by means of the standard methods of microanalysis. A summary of the analyses is contained in Table I.

Determination of the Physical Constants (see Table I).—Phosphorus(III) β-chloroethoxy dichloride and phosphorus(III) β-chloroethoxy difluoride are colorless in the vapor and liquid states. Upon freezing, these compounds

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(1) Presented at the XII International Congress of Pure and Applied Chemistry, New York, N. Y., September 10–13, 1951.

(2) Naval Research Laboratory, Washington, D. C.

(3) Deceased.

(4) D. R. Martin and P. J. Pizzolato, THIS JOURNAL, **72**, 4584 (1950).

(5) D. R. Martin and Leona S. Mako, *ibid.*, **73**, 2674 (1951).

(6) M. I. Kabachnik and P. A. Rossiĭskaya, *Izvest. Akad. Nauk S. S. S. R., Otdel Khim. Nauk*, 295 (1946).

(7) N. Menschutkin, *Ann.*, **139**, 343 (1866).

(8) H. S. Booth, D. R. Martin and F. E. Kendall, THIS JOURNAL, **70**, 2523 (1948).

(9) H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

(10) H. S. Booth and A. R. Bozarth, THIS JOURNAL, **61**, 2927 (1939).

TABLE I

		$ClC_2H_4OPCl_2$	$ClC_2H_4OPF_2$
Boiling point (calcd.) ± 0.1,		162.4	82.7
Freezing point ± 1.0,		−142	−88
Liquid density, dt_4		1.515 (0°)	1.3 (59) (25°)
Vapor pressure constants[a]	A	7.3310	7.8826
	B	1938.4	1780.0
Heat of vaporization, g. cal./mole		8897	8135
Trouton's constant		20.4	22.9
Carbon, %	theory	13.24	16.16
	found	13.08	16.34
Hydrogen, %	theory	2.21	2.69
	found	2.28	2.67
Phosphorus, %	theory	17.10	20.88
	found	17.49	19.75
Chlorine, %	theory	58.62	23.87
	found	58.52	23.31
Molecular weight	theory	...	148.5
(vapor density)	found	...	150
Corrosion,[b] 10^6 in./month		0.22	1.8
Solubilities	Water	Vigorous reaction	Slowly hydrolyzes
	Ethanol	Vigorous reaction	Soluble
	Propylene glycol	Vigorous reaction	Soluble
	Dioxane	Soluble	Soluble
	Acetone	Soluble	Soluble
	Diethyl ether	Soluble	Soluble

[a] $\log p$ (mm.) $= A - B/T$. [b] $c = 43.9\ W/ASt$, in which c, corrosion in in./mo.; W, weight loss in grams; A, area in square inches; S, density in grams/ml. and t, time in hours.

are transformed into white solids. The freezing points were observed by the procedure described by Booth and Martin.[11] The liquid densities were determined with a special pycnometer by the method reported by Booth and Hermann.[12]

The vapor pressures were measured by the static method of Booth, Elsey and Burchfield,[13] and the necessary temperature and pressure corrections have been applied. The equations representing the straight lines in a plot of log p *vs.* $1/T$ were calculated by the method of least squares. From these equations the values for the boiling points, heats of vaporization and Trouton's constants were calculated. The vapor density was determined by the Regnault procedure.

The solubility studies were made at room temperature by adding three to five volumes of solvent to one volume of the phosphorus(III) compound. The qualitative observations are listed in Table I.

The extent of the corrosion of stainless steel in contact with these liquids at room temperature was determined by the standard static corrosion test described by Perry.[14]

Discussion

Phosphorus(III) β-chloroethoxy dichloride and phosphorus(III) β-chloroethoxy difluoride fume in moist air and react with water, the ease of hydrolysis being greater with the dichloride than with the difluoride. This behavior is similar to that shown by the halides of the non-metals which contain no alkoxy radical, *e.g.*, phosphorus(III) chloride and phosphorus(III) fluoride,[10] but is the opposite to that shown by phosphorus(III) methoxy dichloride and its fluoride.[4]

Contrary to the observations of Kabachnik and Rossiĭskaya[6] that phosphorus(III) β-chloroethoxy dichloride was stable thermally up to 190°, its vapor pressure was not reproducible at temperatures exceeding 100°. Evidence of decomposition was the formation of the characteristic yellow-orange solid at higher temperatures. No thermal decomposition of the difluoride at a temperature of 70° was observed.

While the difluoride exhibits a precise freezing point, the dichloride exhibits two distinct crystalline phases. The phase possessing the higher melting point was obtained only upon warming the phase with the lower melting point to room temperature. It was not possible to identify the crystal system to which each phase belonged, nor to determine the transition temperature.

The fluorination of phosphorus(III) β-chloroethoxy dichloride by the Swarts reaction proceeds smoothly and rapidly at room temperature without a catalyst. The course of the reaction is in accord with the rule that a single chlorine atom on a carbon atom is not displaced by a fluorine atom, using antimony(III) fluoride as the fluorinating agent. Fluorine exchange for a chlorine atom which is bonded to a phosphorus atom takes place rapidly and completely as reported earlier.[10] Numerous attempts, using different experimental conditions, to isolate phosphorus(III) β-chloroethoxy chlorofluoride were unsuccessful. Apparently the chlorofluoride is converted easily to difluoride by antimony(III) fluoride. These observations agree with the conclusion of Martin and Pizzolato[4] that the substitution of an alkoxy radical for a chlorine atom in phosphorus(III) chloride produces a more reactive molecule.

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(11) H. S. Booth and D. R. Martin, THIS JOURNAL, **64**, 2198 (1942).

(12) H. S. Booth and C. V. Herrmann, *ibid.*, **58**, 63 (1936).

(13) H. S. Booth, H. M. Elsey and P. E. Burchfield, *ibid.*, **57**, 2064 (1935).

(14) J. H. Perry "Chemical Engineers' Handbook," 3rd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1950 pp. 1458, 1459.