The values of K_c are as constant as one might expect considering the assumption of constancy of all activity coefficients in going from molar ammonium perchlorate to molar ammonium acetate. In addition, the calculation does not take into account the possible formation of undissociated lead acetate of higher complexes. It certainly seems, nevertheless, that the chief reaction involved in the increased solubility of an insoluble lead salt in acetate solution is the formation of the $PbC_2H_3O_2^+$ ion.

Summary

1. Solubilities have been measured for lead iodate in mixtures of ammonium acetate and ammonium perchlorate of unit ionic strength.

2. The results are in agreement with the conclusion that the reaction involves the formation of the ion $PbC_2H_3O_2^+$.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

The Fluorination of Thiophosphoryl Trichloride: The Thiophosphoryl Chlorofluorides[1]

BY HAROLD SIMMONS BOOTH AND MARY CATHERINE CASSIDY

Booth and Swinehart[1a] have shown that antimony trifluoride in the presence of a catalyst such as antimony pentachloride[2] causes the stepwise fluorination of various non-polar halides. It has been shown by Booth and Herrmann[3] that sulfuryl chloride, and by Booth and Mericola[4] that thionyl chloride, can be fluorinated by this reaction without reaction of the sulfur with the antimony fluoride. However, sulfur monochloride failed to be fluorinated by this reaction but instead the sulfur reacted with the antimony fluoride to give a mixture of reaction products.[5] This reaction has been applied by Booth and Dutton[6] to phosphoryl trichloride to yield three fluorination products.

In the light of these investigations it seemed of interest to determine whether thiophosphoryl chloride would react with antimony trifluoride in the presence of antimony pentachloride, in a manner similar to phosphoryl chloride or to sulfur monochloride.

In the former case three products would result; thiophosphoryl dichloromonofluoride, thiophosphoryl monochlorodifluoride and thiophosphoryl trifluoride. The last named was prepared by T. Thorpe and J. Rodgers[7,8] by four different methods: (1) by heating a mixture of phosphorus sulfide and lead fluoride in a current of dry nitrogen in a lead tube at not over 250°, (2) at a little higher temperature, by substituting bismuth fluoride as a fluorinating agent in place of lead fluoride in the above method, (3) by heating sulfur, phosphorus and lead fluoride, (4) by heating thiophosphoryl chloride and sulfur in a sealed tube at 150.

C. Poulenc[9] in 1891 obtained a gas of peculiar and disagreeable odor, that corresponded when analyzed to the formula PSF_3, by heating a mixture of phosphorus dichlorotrifluoride and sulfur at 115° and later in the same year by heating phosphorus dichlorotrifluoride with antimony trisulfide.[10]

More recently (1938) Willy Lange[11] prepared thiophosphoryl fluoride by the method recommended by Thorpe and Rodgers. Although he was chiefly interested in its hydrolysis products, he determined some other properties.

Experimental

The fluorination of thiophosphoryl chloride was effected in a generator that has been described in detail by Booth and Bozarth.[12] When antimony pentachloride, the catalyst, was run into the thiophosphoryl chloride in the generator considerable heat was evolved and a heavy precipitate appeared which redissolved to some extent on stirring. After the temperature of the mixture in the generator had reached 75 to 80°, sublimed antimony trifluoride was slowly added.

Although all three fluorination products were formed

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[1] From a portion of a thesis submitted by Mary Catherine Cassidy in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry to the Graduate School of Western Reserve University, May, 1939. [Original manuscript received November 13, 1939.]

[1a] Booth and Swinehart, THIS JOURNAL, **54**, 4751 (1932).

[2] F. Swarts, *Acad. roy. Belg.*, **24**, 309, 474 (1892).

[3] Booth and Herrmann, THIS JOURNAL, **58**, 62 (1936).

[4] Booth and Mericola, *ibid.*, **62**, 640 (1940).

[5] Unpublished investigation from this Laboratory by Charles Seabright.

[6] Booth and Dutton, THIS JOURNAL, **61**, 2937 (1939).

[7] T. Thorpe and J. Rodgers, *J. Chem. Soc.*, **53**, 766 (1888).

[8] T. Thorpe and J. Rodgers, *ibid.*, **55**, 306 (1889).

[9] C. Poulenc, *Compt. rend.*, **113**, 75 (1891).

[10] C. Poulenc, *Ann. chim. phys.*, [6] **24**, 548 (1891).

[11] Willy Lange, *Ber.*, **71**, 801 (1938).

[12] Booth and Bozarth, THIS JOURNAL, **61**, 2927 (1939).

during each generation, any one product could be made in excess by controlling the temperature of the refluxing head and the pressure at which the products were taken off. Air, ice and dry-ice–acetone mixture were each used in the head, depending on whether thiophosphoryl dichloromonofluoride, thiophosphoryl monochlorodifluoride, or thiophosphoryl trifluoride was desired. As higher fluorine content was desired the pressure was increased from 200 mm. to atmospheric pressure.

Under all conditions of temperature and pressure used, the fluorination proceeded rapidly at first, then gradually slowed.

Purification.—The purification of each of the two gases was accomplished by repeated distillation to constant physical properties in a fractionating column, described in detail by Booth and Bozarth.[13]

A nichrome spiral was used in the column in place of copper since preliminary tests had shown the former was not acted upon by the substances being purified. When thiophosphoryl fluoride was distilled, a liquid air head was used; when thiophosphoryl monochlorodifluoride was distilled a dry-ice–acetone head was substituted.

The liquid, thiophosphoryl dichloromonofluoride, was distilled in a bead-filled column 90 cm. long. The column was equipped with a liquid-divider stillhead and heated externally by a nichrome wire heater.

Anal.—Samples of the liquid, thiophosphoryl dichloromonofluoride, and the high boiling gas, thiophosphoryl monochlorodifluoride, were taken in small glass bulbs and absorbed in 0.5 *N* potassium hydroxide solution as described by Booth and Dutton.[6]

Hydrolysis of compounds of this type takes place slowly according to Willy Lange,[14] so each sample was digested on a water-bath for at least fifty hours. Hydrogen peroxide was then added to oxidize the sulfur to sulfate.

In the case of the low boiling thiophosphoryl fluoride a gas sample was taken in a bulb of about one hundred cubic centimeters capacity, and absorbed in potassium hydroxide solution as described by Booth and Swinehart.[15]

Chlorine was determined gravimetrically as silver chloride; sulfur as barium sulfate; phosphorus was precipitated first as the phosphomolybdate then reprecipitated as magnesium ammonium phosphate and finally ignited to the pyrophosphate. No attempt was made to determine fluorine because of the inadequacy of all known methods, although its presence was established qualitatively.

TABLE I

ANALYSIS

		Phosphorus	Sulfur	Chlorine
$PSFCl_2$	Calcd.	20.28	20.96	46.34
	Found	20.17	20.88	46.63
		20.29	20.74	46.19
PSF_2Cl	Calcd.	22.73	23.48	25.97
	Found	22.77	23.37	26.13
		22.53	23.25	25.78
PSF_3	Calcd.		26.70	
	Found		26.52	
			26.66	

Physical Properties.—Freezing points of thiophosphoryl dichloromonofluoride, thiophosphoryl monochlorodifluoride, and thiophosphoryl fluoride were determined and that of thiophosphoryl chloride was rechecked by the standard method in use in this Laboratory.[13]

Two crystal forms of thiophosphoryl chloride were observed. Usually, on cooling, the lower freezing one, which we shall call the alpha modification, freezing at −40.8 ± 0.2°, formed first. On the removal of the cooling jacket, the transparent crystals changed suddenly to an opaque form, called for convenience the beta form. At the same time an evolution of heat was indicated on the recording potentiometer. This change was not unlike that which happens when monoclinic sulfur needles become opaque on slowly changing to the rhombic form. If now the whole was warmed, but not entirely melted, and then cooled again, a different and higher freezing point was obtained, that is, the freezing point of the beta form, −36.2 ± 0.2°.

Nothing unusual was noticed in the behavior of the other three compounds. In the case of thiophosphoryl chloride and thiophosphoryl dichloromonofluoride, undercooling was observed which was considered as an additional indication of purity.

The liquid density of thiophosphoryl dichloromonofluoride and thiophosphoryl monochlorodifluoride at 0° was determined in a special pycnometer described by Booth and Herrmann.[3]

The gas density in the case of thiophosphoryl monochlorodifluoride and the trifluoride was determined in a gas density balance.[13] In the case of the relatively high boiling thiophosphoryl dichloromonofluoride, the gas density was determined by Regnault's balloon method.

The vapor pressure of the two gases, thiophosphoryl monochlorodifluoride and the thiophosphoryl trifluoride was determined as described by Booth and Bozarth.[13] The vapor pressure of the liquid, thiophosphoryl dichloromonofluoride was measured in the isoteniscope.[16]

A platinum resistance thermometer, calibrated by the United States Bureau of Standards, was used in the determination of the temperature of the bath. All observed pressures are corrected to 0° and standard gravity as given in the "International Critical Tables."

Determination of Critical Constants.—The critical constants of thiophosphoryl monochlorodifluoride and thiophosphoryl trifluoride were determined in the apparatus and as described by Booth and Swinehart.[17] Since thiophosphoryl chloride was known to react with mercury when heated, it was thought advisable to make a pre-

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(13) Booth and Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

(14) Willy Lange, *Ber.*, **62**, 793 (1929).

(15) Booth and Swinehart, THIS JOURNAL, **57**, 1333 (1935).

(16) Booth, Elsey and Burchfield, *ibid.*, **57**, 2064 (1935).

(17) Booth and Swinehart, *ibid.*, **57**, 1337 (1935).

TABLE II

Temp., °C.	P obsd., mm.	P calcd., mm.	Deviation, mm.
Vapor Pressure of $PSFCl_2$, log p = 7.6596 − (1613.9/T)			
−28.6	11.5	11.4	0.1
−17.4	22.5	22.2	.3
− 8.6	36.4	35.9	.5
63.4	731.1	728.1	3.0
64.9	765.2	765.4	−0.2
Vapor Pressure of PSF_2Cl, log p = 7.5100 − (1292.7/T)			
A[a] −66.7	17.9	17.5	0.4
A −57.4	32.9	32.6	.3
B[a] −51.8	44.8	46.3	−1.5
A −47.7	59.8	59.2	0.6
B −34.6	120.5	122.3	−1.8
A −34.1	124.6	125.6	−1.0
A −24.6	202.3	202.3	0.0
B −18.1	272.2	274.5	−2.3
A −13.5	338.8	337.7	1.1
B − 8.9	411.4	412.4	−1.0
B − 5.7	473.2	472.0	1.2
A 0.0	595.6	595.4	0.2
B .8	615.7	614.8	.9
A 3.5	684.3	683.6	.7
B 4.6	712.3	713.4	−1.1
B 5.1	725.2	727.3	−2.1
A 5.8	747.4	747.2	0.2
A 8.3	819.0	821.5	−2.5
Vapor Pressure of PSF_3, log p = 7.5882 − (1038.8/T)			
B −112.1	13.5	13.6	−0.1
B −105.7	23.4	24.1	− .7
B − 95.4	55.3	54.8	.5
A − 90.7	79.7	77.6	2.1
B − 87.0	103.7	101.5	2.2
B − 83.4	132.6	128.6	4.0
A − 79.7	168.9	163.7	5.2
A − 76.5	204.3	199.0	5.3
B − 58.9	545.3	544.8	0.5
A − 57.3	594.7	591.8	2.9
B − 52.5	750.3	753.4	−3.1
A − 51.8	776.1	775.9	0.2
B − 51.3	791.8	798.9	−7.1

[a] Samples A and B were taken from different distillations. Calculated values were obtained from the equations.

liminary test as to the possibility of running the critical constants of thiophosphoryl monochlorodifluoride and dichloromonofluoride. Samples of these two compounds were sealed with mercury in heavy walled tubes and heated to the critical temperature calculated from the boiling point by the "three-halves" rule. The dichloromonofluoride reacted to form a yellow solid; the monochlorodifluoride yielded only a slight white film. For this reason, no attempt was made to determine the critical constants of thiophosphoryl dichloromonofluoride.

Discussion

In some properties the thiophosphoryl chlorofluorides resemble those of the trichloride and the trifluoride while in others a gradation can be observed as the fluorine content increases. All the compounds are colorless, do not attack nichrome, nor mercury if cold, but react slightly with copper; they react completely but slowly with potassium hydroxide solution. With the exception of thiophosphoryl chloride they hydrolyze readily in moist air. With the exception of the fluoride they have practically the same liquidus range. A gradation of properties can be seen when the boiling points or liquid densities are compared.

Considerable difficulty was encountered in preparing pure thiophosphoryl fluoride. Some flocks of silicon tetrafluoride were seen in the liquid gas after each generation, even though elaborate precautions were taken to remove all moisture from the starting materials. The impurity is thought to have been removed, as breaks in the melting point curve became sharper after each distillation and the vapor pressure curve was a straight line.

The statement in the literature that the trifluoride is spontaneously inflammable at room temperature and is explosive if mixed with moist

TABLE III

PHYSICAL PROPERTIES OF FLUORINATION PRODUCTS

	$PSFCl_2$	PSF_2Cl	PSF_3
Boiling point, °C.	64.7 ± 0.05	6.3 ± 0.05	− 52.3 ± 0.05 − 52.6[a]
Freezing point, °C.	−96.0 ± 0.5	−155.2 ± 0.5	−148.8 ± 0.5
Liquid density at 0°C.	1.590	1.484	
Gas density observed	169.1	137.3	121.4
Gas density theoretical	153.0	136.6	120.1
Critical temperature, °C.		166.0	72.8
Critical pressure, atm.		40.9	37.7
Heat of vaporization,[b] cal.	6863	5703	4684
Trouton constant	20.3	20.4	21.2

[a] Willy Lange, ref. 11. [b] Calculated by the Clausius–Clapeyron equation.

air in an enclosed space was corroborated several times by accident. While thiophosphoryl chlorofluorides and thiophosphoryl trichloride do not catch fire when brought in contact with air at room temperature, vapors of thiophosphoryl trichloride escaped on one occasion from a distilling flask and ignited spontaneously. This leads one to wonder whether the intermediate products would ignite spontaneously under the proper conditions.[18]

On cooling, thiophosphoryl monochlorodifluoride condenses to a colorless liquid that becomes more and more viscous until it sets as a glass. The glass quickly changes to an opaque crystalline mass when the Dewar jar of liquid air is removed from it. This might suggest two forms although there was no indication of them from the melting point studies and probably merely means unusually great supercooling.

Thiophosphoryl dichloromonofluoride was distilled in a column open to dry air which it dissolved and held firmly. Considerable difficulty was encountered in removing all the air from the sample used in vapor pressure determinations. However, there was no sign of spontaneous combustion at the condensing point in the column.

Summary

The fluorination of thiophosphoryl chloride by antimony trifluoride in the presence of antimony pentachloride as catalyst yields thiophosphoryl fluoride, and two new compounds, thiophosphoryl monochlorodifluoride and dichloromonofluoride. The physical and a few chemical properties of these three compounds have been determined. It was found that in the solid state thiophosphoryl chloride exists in two forms, the alpha freezing at $-40.8°$ and the beta with a freezing point of $-36.2°$. The alpha form on warming tends to change to the beta form in the solid state. At certain concentrations in air PSF_2Cl is spontaneously explosive.

CLEVELAND, OHIO RECEIVED JUNE 28, 1940

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(18) Since writing this, a storage balloon of 15 l. capacity containing PSF_2Cl at less than one atmosphere pressure developed a leak permitting entrance of air. Finally the balloon exploded violently with sufficient force to demolish a glass lamp reflector 20 feet away. Fortunately, no one was near. Apparently, despite the fact that the gas did not burn on escaping into the air during a previous test, at the right ratio of air to PSF_2Cl it constitutes a dangerous spontaneous explosive.

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Thermodynamic Properties of the Hexyl Alcohols. V. 2,2-Dimethylbutanol-1 and 2-Ethylbutanol-1

BY FRANK HOVORKA, HERMAN P. LANKELMA AND W. RUSLER SMITH

This paper represents the fifth[1] of a series of investigations being carried out in this Laboratory dealing with the relation between the structure and certain physical properties of the isomeric hexyl alcohols, and concerns the vapor pressure, viscosity, surface tension, density and refractive index of 2,2-dimethylbutanol-1 and 2-ethylbutanol-1.

Experimental

Preparation of Materials.—2,2-Dimethylbutanol-1 was prepared from *t*-amyl chloride and formaldehyde by the Grignard synthesis. 2-Ethylbutanol-1 was obtained from Sharples Solvents Corporation and further purified.

Purification.—The fractionating column employed for the distillation of the alcohols has been described previously.[1b]

The alcohols were allowed to stand over Drierite for at least two weeks, filtered and then fractionally distilled. A fraction boiling over a range of 0.02° was taken for the physical measurements.

Apparatus and Procedure.—The apparatus and the procedures used in this research have been described by Hovorka, Lankelma and Stanford.[1b]

The instruments used for the determination of density, surface tension and viscosity were recalibrated before the measurements were made.

Discussion of Results

Vapor Pressure.—The vapor pressure data are tabulated in Table I, column 5.

A summary of the values calculated from the vapor pressure data is given in Table II.

Viscosity.—The viscosity data are collected in Table I, column 3. A discussion of the various theories of viscosity advanced by Andrade,[2] Raman[3] and others has been given before.[1b] These theories need not be discussed further here.

In order to compare the hexanols under con-

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(1) (a) Hovorka, Lankelma and Naujoks, THIS JOURNAL, **55**, 4820 (1933). (b) Hovorka, Lankelma and Stanford, *ibid.*, **60**, 820 (1938). (c) Hovorka, Lankelma and Axelrod, *ibid.*, **62**, 187 (1940). (d) Hovorka, Lankelma and Schneider, *ibid.*, **62**, 1096 (1940).

(2) E. N. Andrade, *Phil. Mag.*, **17**, 497, 698 (1934).

(3) C. V. Raman, *Nature*, **111**, 532 (1923).