of the vibrations of these models has been given by Kohlrausch.[18] The agreement between the calculated forms and frequencies and those observed in the model is not bad, except that Trenkler's form ω_8 has more motion in the meta carbon atoms than does form ξ_3, and its frequency is completely out of line with both calculated and observed values.

Summary

The approximate vibrational forms and frequencies of the Class A_1 carbon vibrations of toluene have been calculated, using a simplified valence-force potential system and force constants from benzene and ethane. The calculated vibrations have been compared with spectral frequencies and with the vibrations of mechanical models. The results have been interpreted so as to *indicate* the following:

1. The observed 623 cm.$^{-1}$ frequency of toluene *does not* belong to a Class A_1 carbon vibration.
2. The 520, 786, 1003 and 1210 cm.$^{-1}$ observed frequencies of toluene belong to Class A_1 carbon vibrations.
3. The 1029 and 1379 cm.$^{-1}$ frequencies of toluene belong to symmetric hydrogen-bending vibrations.
4. Two of the Class A_1 carbon vibrations of toluene are not active in either the Raman or the near-ultraviolet absorption spectra.

BATON ROUGE, LA. RECEIVED MARCH 16, 1948

---

(18) Kohlrausch, *Physik. Z.*, **37**, 58 (1936).

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

Fluorination of Thiophosphorylethoxydichloride[1]

BY HAROLD SIMMONS BOOTH, DONALD RAY MARTIN[2] AND FRED E. KENDALL[3]

Inasmuch as thiophosphoryl trichloride has been stepwise fluorinated in this Laboratory[4] to give thiophosphoryl chlorofluorides and trifluoride, it was of interest to study the effect of substituting an ethoxy group for a chlorine atom upon the fluorination reaction. Therefore, the fluorination of thiophosphorylethoxydichloride by the Swarts reaction was undertaken.

Experimental

Preparation and Purification of Thiophosphorylethoxydichloride.—The thiophosphorylethoxydichloride was prepared by a modification of the directions given by Pishchimuka[5] from thiophosphoryl trichloride and dried, redistilled absolute ethyl alcohol. The thiophosphoryl trichloride was a C. P. (chemically pure) grade obtained from the Victor Chemical Company which was then fractionally distilled.

Two hundred grams of thiophosphoryl trichloride was placed in a three-necked flask fitted with a stirrer, drying tube and a separatory funnel containing 100 g. of absolute ethyl alcohol. The alcohol was added dropwise over a period of two to three hours, care being exercised that the temperature of the reactor did not exceed 10°[6] thus reducing the yield. The crude thiophosphorylethoxydichloride was fractionated once under a pressure of 70 mm. and 4 times under a pressure of 25 mm. in a Raschig ring-packed electrically heated column to give a 70% yield of the purified product.

Fluorination of Thiophosphorylethoxydichloride.—The method and apparatus used for the stepwise fluorination, using the Swarts reaction,[7] was the same as that described elsewhere,[8,9] except that, owing to the high boiling points of the products, an air-cooled condenser was substituted for the usual water-cooled condenser. In order to obtain the chlorofluoride, the fluorination products were removed with an automatic stopcock set to maintain a pressure of 20–30 mm. in the generator. The temperature of the generator must be at, or below, 50° to prevent decomposition of thiophosphorylethoxydichloride and thiophosphorylethoxychlorofluoride. In exploratory fluorination reactions, it was observed that simple addition of antimony trifluoride to thiophosphorylethoxydichloride in a flask, open to the atmosphere through a drying tube, produced about the same results providing the temperature of the reactor was kept below 50°. Little or no reaction was observed when the fluorination was attempted without antimony pentachloride as the catalyst.

Purification of Thiophosphorylethoxydifluoride.—The fluorination products were fractionally distilled in a modified Dufton column as described by Booth and Bozarth.[10] The best coolant for the column head was water, cooled by ice and salt. Samples, from separate generations, were collected by distillation at two different operating pressures, namely, 60 and 100 mm., and found to be identical. The tailings in the still pot had such a low vapor pressure that their distillation in this type of fractionating column was not possible.

Purification of this compound was first attempted with the heated column used to purify the starting material. The distillation was attempted at atmospheric pressure with the receiver open to the atmosphere through a drying tube. However, a reaction of a volatile product with the atmosphere outside the drying tube was observed so this method of purification was abandoned.

Purification of Thiophosphorylethoxychlorofluoride.—The tailings of the above distillations were placed in the heated column used for the purification of thiophosphorylethoxydichloride and were fractionally distilled at pressures of 25 and 70 mm. These samples were found to be

---

[1] From a thesis presented by Fred E. Kendall to the Graduate School of Western Reserve University, February, 1943, in partial fulfillment of the requirements for the degree of Doctor of Philosophy and based upon work done in connection with a research project sponsored by the Naval Research Laboratory, Office of Research and Inventions, U. S. Navy Department. Publication delayed for security reasons.

[2] Present address: Department of Chemistry, University of Illinois, Urbana, Illinois.

[3] Present address: The Master Builders Co., Cleveland, Ohio.

(4) H. S. Booth and M. C. Cassidy, THIS JOURNAL, **62**, 2369–2372 (1940).

(5) P. S. Pishchimuka, *Ber.*, **41**, 3854–3859 (1908); *J. Russ. Phys. Chem. Soc.*, **44**, 1406–1554 (1912).

(6) E. Clemmensen, U. S. Patent 1,945,183, Jan. 30, 1934 (to Monsanto Chemical Co.).

(7) F. Swarts, *Acad. roy. Belg.*, **24**, 309 (1892).

(8) H. S. Booth and C. F. Swinehart, THIS JOURNAL, **54**, 4751–4753 (1932).

(9) H. S. Booth and A. R. Bozarth, *ibid.*, **61**, 2927–2934 (1939).

(10) H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470–475 (1937).

identical. After the removal of the thiophosphorylethoxychlorofluoride, there remained in the still pot a heavy, viscous residue which did not lend itself to subsequent distillation inasmuch as it apparently polymerized at the temperature required to cause vaporization. This material was seemingly resistant to water and organic solvents, but was readily attacked by nitric acid. A similar product forms in the preparation of thiophosphorylethoxydichloride as first observed by Pishchimuka.[5]

Analyses.—The samples weighed in approximately 1-ml. sealed glass ampoules[11] were hydrolyzed in a calculated excess of a 0.5 *N* solution of sodium hydroxide. The hydrolyses were rapid for thiophosphorylethoxydifluoride and thiophosphorylethoxychlorofluoride, but slower for thiophosphorylethoxydichloride. Usually the hydrolytic reactions were allowed to proceed overnight before the samples were treated with hydrogen peroxide to oxidize the sulfide to sulfate. After insurance of the complete removal of excess peroxide, the chlorine was determined by the Volhard method,[11] the sulfur as sulfate gravimetrically[12,13] and the phosphorus volumetrically by precipitating it as ammonium phosphomolybdate which was then dissolved in an excess of 0.25 *N* sodium hydroxide and back-titrated with standardized nitric acid to the phenolphthalein end-point.[12,14,15] Separate samples were hydrolyzed, as described above, and the alcohol fractionally distilled into a tared receiver. The weight of distillate and its density at 25° were used to determine the percentage of ethoxy group present.[16] Fluorine was obtained by difference. A summary of the analyses is contained in Table I.

TABLE I

$C_2H_5OPSX^1X^2$

All compounds are soluble in alcohol, acetone, ether and carbon tetrachloride, but insoluble in water

X^1X^2 are		Cl Cl	Cl F	F F
B. p., °C., 20 mm.		52.0	26.2	78.4[d]
F. p., °C.		−78.4 ±0.5	−178 ±1.0	−124 ±0.5
Vapor pressure constants[a]	*A*	−2108.1	−1984.7	−1700
	B	7.7846	7.9320	7.7174
Variation[b]	Av. ±	0.4	0.7	1.1
	Max.	+1.5	+2.5	−2.7
Liquid $d^0{}_4$		1.4395	1.3828	1.3019
Heat of vaporization, cal.		9647	9082	7779
Corrosion,[c] 10^4 in./month		5.66	1.18	1.26
Percentage compositions, %: Sulfur	Calcd.	17.91	19.72	21.94
	Found	17.76 17.87	19.65 19.70	22.02 22.07
Phosphorus	Calcd.	17.32	19.06	21.20
	Found	17.12 17.18	18.90 18.98	20.97 21.01
Chlorine	Calcd.	39.62	21.80	...
	Found	39.58 39.65	21.65 21.70	... ..
C_2H_5O	Calcd.	23.80	27.69	30.84
	Found	23.50 23.68	27.44 27.50	30.33 30.60

[a] Constants in the equation $\log p$ (mm.) $= (A/T) + B$. [b] Variation in vapor pressure in mm. [c] Corrosion $= C = 43.9W/ASt$. [d] At 760 mm. pressure.

Determination of Physical Constants (see Table I).—The freezing points of separately generated and fractionally distilled samples of these compounds were determined as described by Booth and Martin.[17] In the determination of the freezing points of the dichloride and the difluoride, supercooling was observed to the extent of 12.6 and 10.5°, respectively. The freezing point of thiophosphorylethoxychlorofluoride was difficult to obtain due to a tendency toward glass formation. Further cooling of the glass produced a crystalline product which gave a very short, but reproducible, break in the cooling curve. The transformation from the glass to the crystalline solid was accompanied by a crackling noise and frequently the freezing point cell was broken. Attempts to obtain a melting point were unsuccessful.

Liquid densities were determined at 0° using the method of Booth and Hermann.[18] Qualitative solubility tests were made by adding each compound dropwise to comparable volumes of solvents and allowing the components to stand in contact with each other without stirring for thirty minutes. Except for water, complete miscibility with the solvent was observed immediately upon contact.

The vapor pressures were determined by the static method of Booth, Elsey and Burchfield.[19] The equations in Table I are derived from the original vapor pressure data.

Discussion

Thiophosphorylethoxydichloride was described by Pischimuka[5] as being an oily, clear liquid, possessing a peculiar odor. The liquid density and the boiling point reported by Pischimuka[5] are in poor agreement with the values reported in this study which may be due to impurities in the product obtained by Pischimuka due to reactions described by Cloez[20] and Chevrier.[21] The determination of the vapor pressure of this compound was not possible above 90° because it decomposes into a more volatile constituent. In air and in water, thiophosphorylethoxydichloride shows no tendency to hydrolyze. Small amounts of the liquid have no vesicant action upon the hands. No corrosion was observed when the vapors were in contact with mercury and only slight corrosion was measured[22] when steel was kept in contact with the liquid for eighty-four hours at 0° (see Table I).

Thiophosphorylethoxychlorofluoride is a clear liquid with an odor similar to, but sharper than, thiophosphorylethoxydichloride. Upon exposure to air, dense grayish-white clouds of smoke appear which are attributed to oxidation rather than hydrolysis, inasmuch as no reaction was observed when the liquid was placed in water although it did react readily with a 0.5 *N* solution of sodium hydroxide. A similar reaction occurs to a greater extent when the difluoride is exposed to the atmosphere. The chlorofluoride in the gaseous state apparently does not attack mercury and its corrosion of steel, as would be expected, is less than that of the dichloride which is very slight as shown in Table I.

Thiophosphorylethoxydifluoride is a clear, highly refractive liquid, having an odor similar to that of the dichloride and chlorofluoride. Voluminous clouds of a grayish-white reaction product are liberated when the difluoride is allowed to mix with the atmosphere. As with the chlorofluoride,

---

(11) H. S. Booth and W. D. Stillwell, THIS JOURNAL, **56**, 1531–1535 (1934).

(12) W. W. Scott, "Standard Methods of Chemical Analysis," Vol. I, 5th ed., D. Van Nostrand Co., Inc., New York, N. Y., 1938.

(13) S. Popoff and E. W. Neuman, *Ind. Eng. Chem., Anal. Ed.*, **2**, 45–54 (1930).

(14) N. H. Furman and H. M. State, *ibid.*, **8**, 420–423 (1936).

(15) W. M. McNabb, THIS JOURNAL, **49**, 891–896 (1927).

(16) O. v. Lupin, *Z. anal. Chem.*, **97**, 210–220 (1934).

(17) H. S. Booth and D. R. Martin, THIS JOURNAL, **64**, 2198–2205 (1942).

(18) H. S. Booth and C. V. Hermann, *ibid.*, **58**, 63–66 (1936).

(19) H. S. Booth, H. M. Elsey and P. E. Burchfield, *ibid.*, **57**, 2064–2065 (1935).

(20) S. Cloez, *Compt. rend.*, **24**, 388–389 (1847).

(21) Chevrier, *ibid.*, **68**, 924–927 (1869); *Z. Chem.*, 413 (1869).

(22) J. H. Perry, "Chemical Engineers' Handbook," 2nd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 2095.

the reaction is believed to be one of oxidation inasmuch as the liquid does not appear to react with water. The fumes have an odor similar to that of ozone. As with the other compounds, little or no reaction with mercury or steel was observed (see Table I).

As expected, the substitution of fluorine for chlorine increases the stability of the compounds in this series. In the determination of the vapor pressures it was observed that the dichloride decomposes around 90°, and the chlorofluoride around 100° whereas the difluoride was observed to be stable up to its normal boiling point, 78.4°.

Although the equations for the vapor pressure of the dichloride and chlorofluoride are reliable only up to around 100°, calculation of the boiling points of these compounds under 760 mm. pressure gives values of 157 and 120°, respectively. Once again the Swarts rule for regular lowering of the boiling point of a compound by substitution of a fluorine atom is valid. One fluorine atom lowers the boiling point from 157 to 120° ($\Delta = 37°$) and the second fluorine substitution cause the boiling point to drop to 78.4° ($\Delta = 42°$).

Acknowledgment.—This investigation was carried out under the sponsorship of the Naval Research Laboratory. We are deeply indebted to members of the staff of the Chemical Division for valuable suggestions and encouragement during its progress.

Summary

Thiophosphorylethoxydichloride was prepared from thiophosphoryltrichloride and ethanol, purified and certain of its physical and chemical properties observed. Upon fluorination, by means of the Swarts reaction with antimony pentachloride as catalyst, thiophosphorylethoxychlorofluoride and thiophosphorylethoxydifluoride were obtained. These new compounds were purified and some of their physical and chemical properties studied.

The properties determined for the above compounds include freezing point, vapor pressure, boiling point, heat of vaporization, Trouton constant, liquid density, solubilities, corrosion tests, and hydrolysis.

CLEVELAND, OHIO RECEIVED MARCH 15, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Polarographic Characteristics of +2 and +3 Vanadium. I. Polarography in Non-complexing Solutions[1]

BY JAMES J. LINGANE AND LOUIS MEITES[2]

Previous papers[3,4] from this Laboratory have discussed the polarography of the +2 and +3 states of vanadium in solutions of dilute acids and of oxalates. In these media the V(II)–V(III) couple is thermodynamically reversible at the dropping electrode. The investigation described in this and a following paper was undertaken to extend the information concerning solutions of these ions and of their complexes. The polarographic characteristics of +2 and +3 vanadium have been studied in a wide variety of media, including dilute acids and alkalies, phosphate, acetate, pyridine, and carbonate buffers, and solutions of the halides, thiocyanate, cyanide, thiosulfate, pyrophosphate, borate, benzoate, phthalate, salicylate, tartrate and citrate. This paper discusses only the cases in which no complex ions are formed. The experimental technique was essentially the same as that used in previous studies.[3,4]

Data and Discussion

We have found the half-wave potential for the reduction of vanadic to vanadous ion in 1 *N* sulfuric, hydrochloric, or perchloric acid to be -0.508 ± 0.002 v. *vs.* the saturated calomel electrode, which agrees very well with the standard potential of the couple reported by Jones and Colvin.[5] Zeltzer's determination of this constant[6] actually corresponds to the half-wave potential of +4 vanadium[3]; his solutions appear to have been quantitatively air-oxidized.

As the concentration of free acid is decreased, the wave becomes somewhat irreversible and shifts to more negative potentials. In 0.002 *N* acid the half-wave potential is −0.59 v. A second small wave at about −0.95 v. develops as the acid concentration is decreased. This wave is due to reduction of the hydrolysis product $V(OH)^{++}$, whose polarographic characteristics are discussed below.

We previously found the anodic half-wave potential of vanadous ion in 1 *N* sulfuric acid to be −0.50 v.,[3] and the corresponding (anodic) diffusion current constant to be -1.74 ± 0.01.[4] Since this constant is much larger than that found for vanadic ion, 1.41 ± 0.01, it follows that aquovanadous ion must be much smaller than aquovanadic ion. The half-wave potential of this anodic wave is not measurably affected by replacing the sulfuric acid with hydrochloric or perchloric acid.

---

[1] This paper is based on a thesis submitted by Louis Meites to the Graduate Faculty of Harvard University in partial fulfilment of the requirements for the degree of Doctor of Philosophy in February, 1947.

[2] Present address: Department of Chemistry, Princeton University, Princeton, N. J.

[3] J. J. Lingane, THIS JOURNAL, **67**, 182 (1945).

[4] J. J. Lingane and L. Meites, *ibid.*, **69**, 1021 (1947).

[5] G. Jones and J. H. Colvin, *ibid.*, **66**, 1563 (1944).

[6] S. Zeltzer, *Coll. Czechoslov. Chem. Commun.*, **4**, 319 (1932).