Trimethylphosphine and Trimethylboron.—Following the above procedure, gaseous trimethylphosphine (1.02 mmoles.) was bubbled through mercury into gaseous trimethylboron (0.94 mmole.). From the first reading (three minutes after the first trimethylphosphine was admitted) until over an hour had elapsed, the pressure in the reaction flask corresponded to 0.09 mmole. of unreacted gas. Since complete reaction would have left 0.08 mmole., the reaction was at least 99.5% complete within the first three minutes.

Summary

1. Contrary to reports in the literature, pure trimethylamine and carbon disulfide do not combine to form an addition compound at temperatures from -80 to 25° and pressures up to 2.5 atm. Under the same conditions, trimethylphosphine and carbon disulfide readily react to form a 1:1 molecular addition compound.

2. Dimethylamine and carbon disulfide readily react in the ratio 2 Me_2NH : 1 CS_2 to form a white solid of low volatility, probably $(Me_2NH_2)^+$-$(Me_2NCS_2)^-$. It is concluded that earlier reports claiming the formation of addition compounds between carbon disulfide and trimethylamine resulted from the presence of dimethylamine in the trimethylamine used.

3. The gas phase reaction of trimethylphosphine with carbon disulfide proceeds at a rate several orders of magnitude slower than the reaction of trimethylphosphine with a typical Lewis "primary" acid, such as trimethylboron.

4. Neither trimethylamine nor trimethylphosphine reacts with carbon dioxide at temperatures down to $-80°$.

LAFAYETTE, INDIANA RECEIVED MARCH 26, 1949

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL OF CANADA AND THE LABORATORIO DE HISTOFISIOLOGIA, FUNDAÇAO ANDREA E VIRGINIA MATARAZZO, SAO PAULO, BRASIL][1]

The Infrared Spectrum of Thiophosphoryl Chloride

BY GIUSEPPE CILENTO,[2] D. A. RAMSAY AND R. NORMAN JONES

Several investigations of the Raman spectrum of liquid thiophosphoryl chloride have been reported in the literature[3–6] but no measurements of its infrared spectrum have hitherto been published. The appearance of three depolarized lines in the Raman spectrum indicates a pyramidal structure for the molecule with symmetry C_{3v}, and this is consistent with the results of electron diffraction investigations.[7] The molecule is therefore a symmetric top and should possess six distinct fundamental frequencies, three totally symmetric (Type A_1) and three doubly degenerate (Type E). These frequencies should be active both in the infrared and in the Raman spectrum.

Six Raman frequencies were reported by Thatte[3] and by Simon and Schulze[4] but Gerding and Westrik[5] reported only five and considered that the sixth Raman shift reported by the former authors at 382 cm.$^{-1}$ corresponded to the strong 435 cm.$^{-1}$ shift excited by the 4347.5 Å. mercury line. These conclusions were confirmed by Delwaulle and François.[6] By comparing the Raman spectra of phosphorus trichloride, phosphoryl chloride and thiophosphoryl chloride, Gerding and Westrik deduced that the sixth frequency for thiophosphoryl chloride should lie in the region of 240 cm.$^{-1}$ and probably be masked by the intense band at 250 cm.$^{-1}$. Similar conclusions were reached by Delwaulle and François by comparing the Raman spectra of thiophosphoryl trichloride, thiophosphoryl bromodichloride thiophosphoryl chlorodibromide and thiophosphoryltribromide. The latter authors pointed out that since the masses of the chlorine and sulfur atoms are approximately the same it is not surprising that the missing P–Cl bending frequency should almost coincide with the P–S bending frequency. A similar coincidence is observed in the Raman spectrum of phosphorus oxyfluoride.

Though it was not possible to observe infrared absorption bands in the region of 250 cm.$^{-1}$ with the facilities at our disposal,[8] an investigation of the infrared spectrum of thiophosphoryl chloride was carried out over the regions accessible with sodium chloride and potassium bromide prisms. This provides a check on the assignment based on the Raman data and it was also anticipated that some evidence concerning the location of the missing frequency might be obtained from an analysis of the combination tones observed at higher frequencies.

Experimental

Thiophosphoryl chloride was prepared by heating phosphorus trichloride and sulfur in stoichiometric proportions in a closed tube at 130° for several hours.[9] The resultant product was distilled several times and the fraction distilling at 114–115° under 700 mm. was used in subsequent

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(1) Published as Contribution 1969 from the Laboratories of the National Research Council of Canada.

(2) Guest Worker of the Division of Chemistry, National Research Council of Canada.

(3) Thatte, *Nature*, **138**, 468 (1936).

(4) Simon and Schulze, *Naturwissenschaften*, **25**, 669 (1937).

(5) Gerding and Westrik, *Rec. trav. chim.*, **61**, 842 (1942).

(6) Delwaulle and François, *Compt. rend.*, **224**, 1422 (1947).

(7) Beach and Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

(8) This frequency is close to the lower limit attainable with a thallium bromide/thallium iodide (KRS-5) prism. See Plyler, *J. Research Natl. Bur. of Standards*, **41**, 125 (1948).

(9) Henry, *Ber.*, **2**, 638 (1869).

TABLE I

INFRARED AND RAMAN FREQUENCIES FOR THIOPHOSPHORYL CHLORIDE

Infrared, cm.$^{-1}$		Raman, cm.$^{-1}$	
Vapor	Liquid	Liquid	Assignment
		169 ($5^1/_2$) dep.	δ(P–Cl) (E)
		247 (7) dep.	δ(P–S) (E)
P ?			
Q **433**	**430** (s)[a]	**432** (10) pol.	ν(P–Cl) (A_1)
R **441**			
	500s (w)		247 + 247 = 494 (A_1 + E)
550	**540** (vs)	**540** (1–2) dep.	ν(P—Cl) (E)
593	590 (w)		169 + 432 = 601 (E)
684	680 (w)		247 + 432 = 679 (E)
715	710s (w)		169 + 540 = 709 (A_1 + E)
P **762**			
Q **768.5**	**751** (vs)	**751** (1–2) pol.	ν(P–S) (A_1)
R **775**			
793s[b]			247 + 540 = 787 (A_1 + E)
865	860 (w)		432 + 432 = 864 (A_1)
934	922 (w)		169 + 751 = 920 (E)
977	964 (w)		432 + 540 = 972 (E)
	984s (w)		247 + 751 = 998 (E)
	1011 (vw)		{ 432 + 751 − 169 = 1014 (E) 260 + 751 = 1011 (A_1)?
1089	1076 (w)		540 + 540 = 1080 (A_1 + E)
1197	1183 (w)		432 + 751 = 1183 (A_1)
1321	1301 (w)		540 + 751 = 1291 (E)
1530	1503 (w)		751 + 751 = 1502 (A_1)

[a] (vs) very strong, (s) strong, (w) weak, (vw) very weak. [b] s denotes partially resolved shoulder. The Raman frequencies are the mean values of those given in references 3–6. The intensity and polarization data are taken from Gerding and Westrik [3]

experiments. The product gave the following analysis.

P calcd.:	18.29	obs.:	18.56	18.94
S calcd.:	18.92	obs.:	18.86	18.90
Cl calcd.:	62.79	obs.:	62.74	62.74

The infrared spectra of the liquid and the vapor were investigated in the region 400 to 1600 cm.$^{-1}$ using a Perkin–Elmer Model 12B infrared spectrometer with sodium chloride and potassium bromide prisms. The liquid spectra were determined in closed cells to prevent hydrolysis of the sample by atmospheric moisture; various cell thicknesses were used for the investigation of the combination and fundamental bands (see Fig. 1). The vapor spectra were measured in a 10-cm. absorption cell with potassium bromide windows; the cell was surrounded by a jacket through which hot vapors could be circulated.[10] By using various pressures up to the saturated vapor pressure of the liquid at 80°, the bands observed in the liquid spectrum were also examined in the vapor phase. The bands were mostly broad and did not reveal any rotational contour except for two of the fundamental bands at 768.5 cm.$^{-1}$ and 433 cm.$^{-1}$ (see Fig. 2). The infrared frequencies for the vapor and the liquid are listed in Table I together with the Raman frequencies of the liquid.

Discussion

The three strong bands in the infrared spectrum of the liquid at 430, 540 and 751 cm.$^{-1}$ are in good agreement with the corresponding Raman fundamentals assigned by Gerding and Westrik. The 430 cm.$^{-1}$ and 751 cm.$^{-1}$ bands exhibit PQR-contours in the vapor spectrum with prominent Q-branches. This is consistent with the assignment of these frequencies to "parallel" vibrations of a symmetric top molecule. The 540 cm.$^{-1}$ band which does not reveal this structure in the vapor phase under similar resolving power is presumably a perpendicular type band.

The value expected for the PR-separation of the "parallel" bands may be calculated using the doublet separation formula of Gerhard and Dennison.[11] Taking the electron diffraction values[7] for the dimensions of the molecule, *viz.*

$$r_{P-S} = 1.94 \pm 0.03 \text{ Å}. \quad r_{P-Cl} = 2.01 \pm 0.02 \text{ Å}.$$
$$\text{Cl-}\hat{\text{P}}\text{-Cl} = 107 \pm 3°$$

the principal moments of inertia of the molecule are

$$I_A = I_B = 296 \pm 115 \times 10^{-40} \text{ g. cm.}^2$$
$$I_C = 615 \pm 60 \times 10^{-40} \text{ g. cm.}^2$$

giving a PR-separation for "parallel" bands at 20° of 18.6 ± 4.2 cm.$^{-1}$. The value observed for the PR-separation of the 768.5 cm.$^{-1}$ band was 13 cm.$^{-1}$; hence the agreement is just within the experimental error of measurement. The contour of the 433 cm.$^{-1}$ band was not sufficiently well resolved to provide a further check on the experimental PR-separation.

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(10) H. J. Bernstein, *J. Chem. Phys.*, **17**, 259 (1949).

(11) Gerhard and Dennison, *Phys. Rev.*, **43**, 197 (1933).

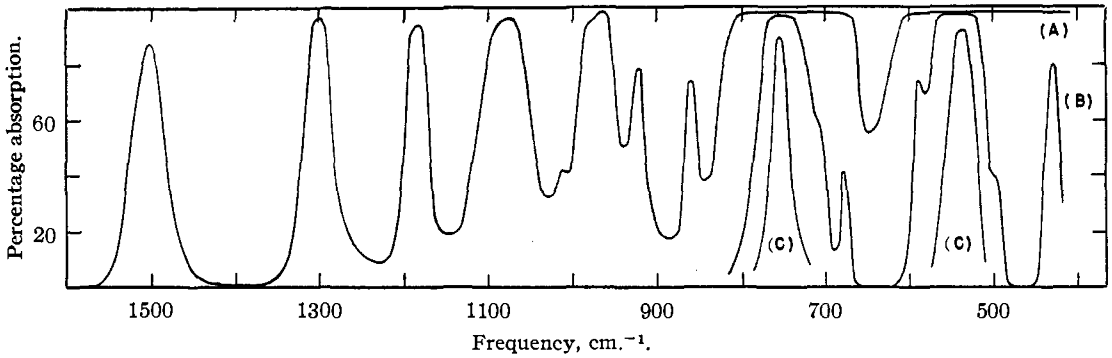

Fig. 1.—Infrared absorption spectrum of liquid thiophosphoryl chloride: (A), 1 mm.; (B), 0.025 mm.; (C), capillary layer.

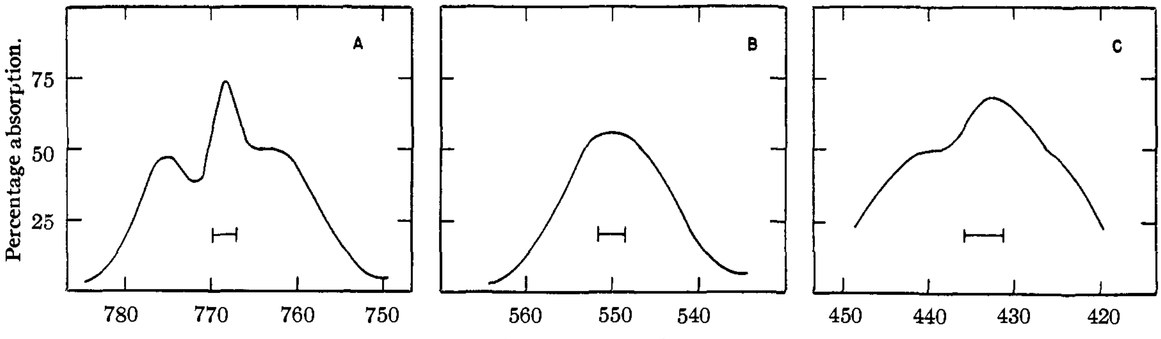

Fig. 2.—Contours of some infrared fundamentals of thiophosphoryl chloride in the vapor phase: cell length, 10 cm.; A and B pressure is ~3 mm., temperature is 20°; C, saturated vapor pressure at 27°.

The contours to be expected for the perpendicular type bands may be obtained by reference to the curves given by Gerhard and Dennison for different values of $\beta = (I_A/I_C) - 1$. For thiophosphoryl chloride $\beta = -0.52$, hence the perpendicular type bands should show PQR-structures with prominent P- and R-branches, the PR-separation being somewhat less than for the "parallel" bands. The 549 cm.$^{-1}$ band, however, showed only a broad contour, hence it is probable that the resolving power of the spectrometer was insufficient to separate the PQR-structure.

In addition to the three fundamentals, fourteen other bands were observed and may be assigned to combination tones. For a symmetric top molecule with symmetry C_{3v} all possible combination tones are permitted to appear in the infrared and in the Raman spectrum,[12] and it is interesting to note that all binary combinations of the five Raman frequencies occurring in the region of the infrared spectrum investigated, have been observed. The only band which cannot be explained in this way is the very weak 1011 cm.$^{-1}$ band. This may be interpreted either as a triple tone ($432 + 751 - 169 = 1014$ cm.$^{-1}$) or possibly as a combination of the 751 cm.$^{-1}$ band with the missing fundamental in the region of 260 cm.$^{-1}$. If the latter interpretation is correct, other combination tones, *e. g.*, (260 + 540), (260 + 432), (260 + 247), might be expected, but these were not observed. The infrared spectrum therefore is consistent with the assignments based on the Raman data, but gives little information concerning the frequency of the missing fundamental.

Acknowledgment.—We wish to thank Mr. A. K. Light of the Analytical Laboratories of the National Research Council for the analyses of the thiophosphoryl chloride, and Dr. H. J. Bernstein for helpful discussions.

Summary

The infrared spectrum of thiophosphoryl chloride in the region 400 to 1600 cm.$^{-1}$ has been investigated both for the liquid and for the vapor. Three fundamental frequencies have been observed and are in good agreement with the corresponding Raman frequencies. Two of the fundamentals show PQR-contours in the vapor spectrum as expected for "parallel" bands of a symmetric top molecule. The PR-separation agrees within the limits of experimental error with the value calculated from the doublet separation formula of Gerhard and Dennison using the accepted electron diffraction values for the bond lengths and angles. Fourteen combination tones

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[12] Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 452.

have been observed, thirteen of which may be satisfactorily explained as binary combinations of the five Raman fundamentals. The remaining combination tone may be a binary combination involving the missing fundamental in the region of 260 cm.$^{-1}$.

Ottawa, Canada
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Received March 21, 1949

[Contribution from the Research Laboratories of the Sprague Electric Company]

Some Reactions of Pentachlorobenzyl Chloride and Pentachlorobenzal Chloride; Steric Hindrance in the Alcoholysis of Pentachlorobenzal Chloride

By Sidney D. Ross and Moushy Markarian

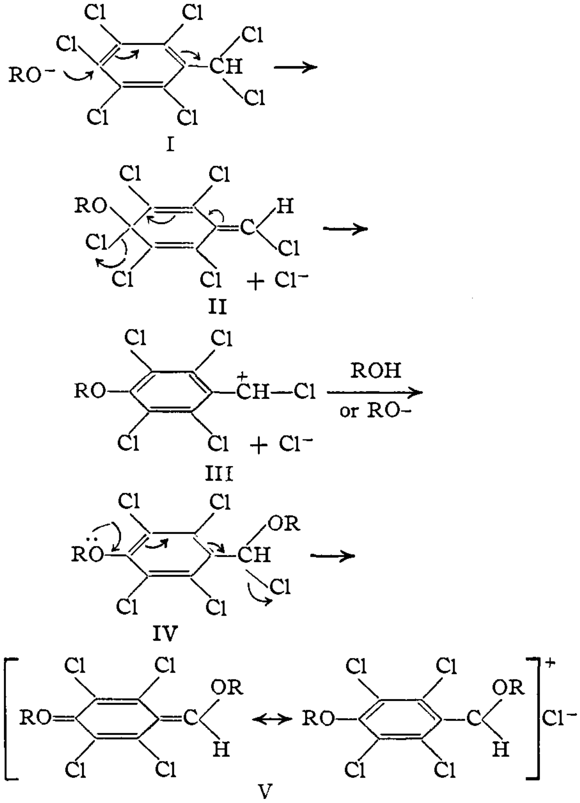
On the basis of earlier studies of substituted benzyl and benzal chlorides,[1] one would expect no great difference in the reactivity of pentachlorobenzyl and pentachlorobenzal chloride. However, the chlorine substituents at the 2- and 6-positions[2] might introduce steric effects, especially so in the case of the benzal derivative with its large $-CHCl_2$ group at the one position. The present work was undertaken to investigate the importance of such steric effects.

Pentachlorobenzyl chloride gave the expected products in the Friedel–Crafts reaction with benzene and in displacement reactions with alkoxide ions and acetate ion. With potassium hydroxide in aqueous acetone, dipentachlorobenzyl ether and 4-pentachlorophenyl-butanone-2 were obtained, and these products probably result from normal, nucleophilic displacements on the benzyl chloride by the conjugate bases of pentachlorobenzyl alcohol and acetone, respectively.

Pentachlorobenzal chloride reacts with benzene in the presence of aluminum chloride to give benzhydrylpentachlorobenzene, but this does not indicate an absence of steric hindrance, for the Friedel–Crafts alkylation involves a front side attack of the catalyst on the covalent carbon–chlorine bond.[3] More significantly, pentachlorobenzal chloride failed to react with either potassium acetate or silver acetate in acetic acid or with potassium hydroxide in aqueous acetone.

On reaction with sodium ethoxide in ethanol, pentachlorobenzal chloride gave, not the expected diethylacetal of pentachlorobenzaldehyde, but a product analyzing correctly for the diethylacetal of an ethoxytetrachlorobenzaldehyde, $C_{13}H_{16}O_3Cl_4$. Hydrolysis of this product gave an ethoxytetrachlorobenzaldehyde, $C_9H_6O_2Cl_4$, which differs from the known 2,4,5,6-tetrachloro-3-ethoxybenzaldehyde.[4] Similar results were obtained with sodium methoxide and sodium isopropoxide. On oxidation with fuming nitric acid the methoxytetrachlorobenzaldehyde gave chloranil, and we have, therefore, assigned 2,3,5,6-tetrachloro-4-alkoxybenzaldehyde structures to the three aldehydes.

The initial attack in the alcoholysis is probably on the para chlorine atom, since no acetals of pentachlorobenzaldehyde were isolated. If we assume such an initial attack, it is possible to rationalize the course of the reaction as



The carbonium ion, V, on reaction with alcohol or alkoxide ion, would give the final product. Such an attack on the para chlorine atom is probable only if there is appreciable steric hindrance about the one position.

Experimental[5]

Pentachlorobenzyl Chloride.—Chlorine was added to molten pentachlorotoluene until the calculated gain in

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[1] The substituted benzyl chlorides have been extensively studied by Olivier (*Rec. trav. chim.*, **42**, 775 (1923); **49**, 697 (1930)) and the benzal chlorides by Asinger and Lock (*Monatsh.*, **62**, 323 (1930)). In both cases the rates of hydrolysis in acetone–water and alcohol–water were measured.

[2] Ross, This Journal, **70**, 4039 (1948).

[3] Fairbrother, *Trans. Faraday Soc.*, **37**, 763 (1941).

[4] Biltz and Tammann, *Ber.*, **34**, 4118 (1901).

[5] The microanalyses are by Dr. Carl Tiedcke.