530. *Far-ultraviolet Absorption Spectra of Phosphorus Compounds in the Gas Phase.*

By M. Halmann.

Ultraviolet absorption spectra at 1850—2500 Å of several simple phosphorus compounds in the gas phase have been observed. All the tervalent phosphorus derivatives absorb strongly in the 2000 Å region, probably owing to $(n \longrightarrow \delta^*)$ transitions, but phosphoryl derivatives have much weaker absorptivity in the same region, assigned as $(n \longrightarrow \pi^*)$ transitions. The intense absorption bands of phosphine (1910 Å), trimethylphosphine (2010 Å), trimethyl phosphite (1890 Å), and phosphorus trichloride (2170 Å) should be useful for their analysis.[1]

In contrast to the extended work on the infrared absorption of phosphorus compounds, only few results have been reported for their spectra in the ultraviolet region.[2-6] Such information is valuable for a better understanding of their electronic structure and chemical reactivity. In the present work the absorption of a number of simple compounds in the gaseous phase was measured in the ultraviolet region down to 1850 Å.

Results

Phosphine.—Absorptivity data for phosphine have previously been reported [3,7] down to 2000 Å and agree with the present results, which extend further, to 1850 Å (see Fig. 1). No

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[1] Preliminary results: Proc. Internat. Symposium on Molecular Structure and Spectroscopy, Tokyo, Japan, September 1962.

[2] Jan-Khan and Samuel, *Proc. Phys. Soc.*, 1936, **48**, *A*, 626; Sponer and Teller, *Rev. Mod. Phys.*, 1941, **13**, 75.

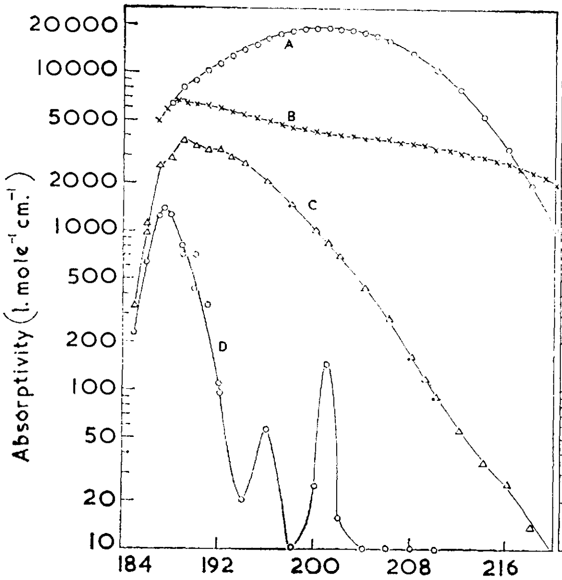
[3] Melville, *Nature*, 1932, **129**, 546.

[4] Milobedzki and Borowski, *Roczniki Chem.*, 1938, **18**, 725; De Hauss, *Chim. Analyt.*, 1952, **34**, 249; Serra and Malatesta, *Ann. Chim.* (*Rome*), 1955, **45**, 911.

[5] Halmann, *J.*, 1954, 2158.

[6] Jaffé, *J. Chem. Phys.*, 1954, **22**, 1430; Jaffé and Orchin, " Theory and Applications of Ultraviolet Spectroscopy," Wiley and Sons, New York, 1962.

[7] Stevenson, Coppinger, and Forbes, *J. Amer. Chem. Soc.*, 1961, **83**, 4350.



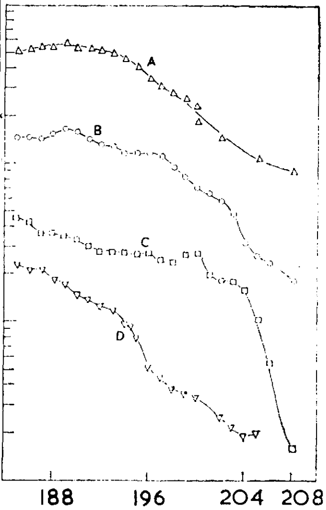


Fig. 1. Fig. 2.

Fig. 1. Ultraviolet absorption of gaseous trimethylphosphine (A), dimethylphosphine (B), phosphine (C), and methylphosphine (D).

Fig. 2. Ultraviolet absorption of gaseous trimethyl phosphite (A), triethyl phosphite (B), diethyl phosphonate (C), and dimethyl phosphonate (D).

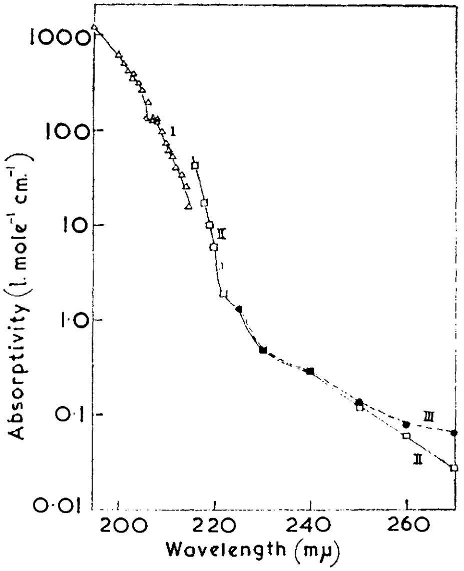


Fig. 3. Ultraviolet absorption of triethyl phosphite in the vapour phase (I), in n-hexane solution (II), and in ethanol solution (III).

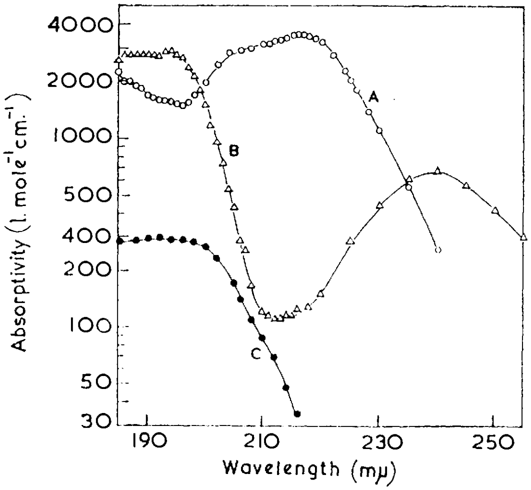


Fig. 4. Ultraviolet absorption of gaseous phosphorus trichloride (A), chlorodiethylphosphine (B), and phosphoryl chloride (C).

vacuum-ultraviolet absorption measurements for phosphine have been reported,† but mass-spectrometric studies [8] on phosphine have provided the following values:

$$PH_3 \longrightarrow PH_3^+ + e;\ \text{ionisation potential} = 10{\cdot}0\ \text{ev}$$

and

$$PH_3^+ \longrightarrow PH_2^+ + H;\ \text{appearance potential} = 13{\cdot}9\ \text{ev}.$$

If we assume the energy requirements for ionisation or dissociation of phosphine by photolysis to be similar to those by electron impact,[9] the threshold for the ionisation continuum would be expected to be below 1300 Å.

Methylphosphines.—The ultraviolet absorption spectra of methyl-, dimethyl-, and trimethyl-phosphine have not yet been reported. As shown in Fig. 1, all these phosphines absorb appreciably in the gas phase below 2200 Å. Trimethylphosphine has a remarkably strong broad absorption maximum at 2010 ± 5 Å with $\varepsilon = 18{,}800$ l. mole^{-1} cm.$^{-1}$, which should be useful for its quantitative determination, even in minute amounts (*e.g.*, after gas chromatography [10]). Methylphosphine has a weak but very sharp absorption maximum at 2010 ± 3 Å. At wavelengths above 2180 Å (not shown in Fig. 1) the absorptivity of all the methylphosphines decreases gradually and no further bands were observed.

Comparison of ultraviolet absorptivities (in l. mole^{-1} cm.$^{-1}$) of phosphines and amines.[11]

	$\lambda_{max.}$ (Å)	ε (l. mole^{-1} cm.$^{-1}$)	$\lambda_{max.}$ (Å)	ε (l. mole^{-1} cm.$^{-1}$)
PH_3	1910	3400 ± 200	NH_3 1942, 1515	5600, strong
$MePH_2$...	2010 ± 3, 1960, 1870	130 ± 30, weak, 1500 ± 200	$MeNH_2$ 2150, 1737	600, 2200
Me_2PH...	1890	6300 ± 500	Me_2NH 2200, 1905	100, 3300
Me_3P ...	2010 ± 5	18,800 ± 100	Me_3N 2273, 1990	900, 3950

In the analogous series of ammonia and the methylamines, measurements of absorptivity down to the vacuum-ultraviolet region have been reported.[11] The results are compared in the Table with ours for the phosphine series (which reach only to 1850 Å). For the methylphosphines, the first (longest-wavelength) absorption maximum is shifted towards shorter wavelength, compared with that of the corresponding methylamine.

Trialkyl Phosphites $(RO)_3P$ *and Dialkyl Phosphonates* $(RO)_2PHO$.—Ultraviolet-absorption measurements of solutions of trialkyl phosphites and dialkyl phosphonates seemed to indicate a strong maximum at about 2600 Å; [4] pure triethyl phosphite was, however, shown not to absorb in this region.[5] The ultraviolet absorptions of gaseous trimethyl and triethyl phosphite and of dimethyl and diethyl phosphonate are given in Fig. 2. Owing to the low vapour pressures of the dialkyl phosphonates, their absorptivity data are less reliable than those of the other compounds. The strong absorptivity of trialkyl phosphites in the 1900 Å region should be useful for analytical purposes, *e.g.*, for their determination in the presence of dialkyl phosphonates.

The absorption spectrum of triethyl phosphite in the gas phase is presented in Fig. 3, together with its spectrum in n-hexane and ethanol.[5] The results in n-hexane have now been extended to 2160 Å and are seen to be (within experimental error) a continuation of the vapour absorption. It is thus concluded that n-hexane solutions contain unassociated molecules of triethyl phosphite.

Phosphorus Trichloride.—Solutions of phosphorus trichloride in ether were reported [4] to have gradually increasing absorptivity from 3100 to 2900 Å. Phosphorus trichloride vapour was stated to absorb very strongly below 2440 Å.[2] The absorption spectrum of phosphorus trichloride vapour in the 2400—1850 Å region has now been measured, and is recorded in Fig. 4. The very pronounced maximum at 2170 ± 5 Å (ε 3500 ± 300 l. mole^{-1} cm.$^{-1}$) should be of considerable analytical use, since this wavelength is easily accessible with most ultraviolet spectrophotometers. At 2070—2040 Å the absorptivity has a plateau. After a minimum at 1960 Å, the absorptivity increases again to another maximum, which is however not yet reached at 1850 Å.

Chlorodiethylphosphine (*Diethylphosphinous Chloride*).—The absorption spectrum of chlorodiethylphosphine, Et_2PCl, is included in Fig. 4. This compound has two broad absorption

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† *Added in proof.* The ultraviolet absorption of phosphine to 1250 Å has now been reported (Walsh and Warsop, *Adv. Mol. Spectroscopy*, 1962, **2**, 582).

[8] Neuert and Clasen, *Z. Naturforsch.*, 1952, **7a**, 410. Stevenson, *Radiation Res.*, 1959, **10**, 610.

[9] Watanabe, *J. Chem. Phys.*, 1954, **22**, 1570.

[10] Halmann, "Chemical Effects of Nuclear Transformations," Proc. Symposium, Prague, Oct. 1960, Internat. Atomic Energy Agency, Vienna, 1961, p. 195.

[11] Tannenbaum, Coffin, and Harrison, *J. Chem. Phys.*, 1953, **21**, 311.

maxima, at 2400 and 1940 Å. By comparison with phosphorus trichloride, its first band is shifted towards longer wavelength by alkyl substitution.

Phosphoryl Chloride.—The vapour of phosphoryl chloride was stated[2] to absorb very strongly below 2200 Å. In the present work (see Fig. 4) phosphoryl chloride was found to have very low absorptivity above 2100 Å, and a broad plateau or maximum at 1960—1850 Å.

DISCUSSION

The electronic excitation responsible for the first (longest-wavelength) absorption bands of phosphines and trialkyl phosphites involves promotion of a non-bonding electron of the phosphorus atom to an antibonding orbital. The intense maxima observed in the 2000—1850 Å region are thus probably of the type ($n \longrightarrow \delta^*$), in analogy with the corresponding transitions in amines and alcohols.[7,12]

The absorption spectrum of phosphorus trichloride shows two strong maxima, at 2170 and below 1850 Å, as well as an unresolved shoulder at 2080 Å. While the two longest wavelength bands seem to be due to ($n \longrightarrow \delta^*$) transitions of orbitals on the chlorine and phosphorus atoms, the intense absorption starting below 1850 Å may possibly be due to a ($\delta \longrightarrow \delta^*$) transition of bonding orbitals.

The weak absorption plateau of phosphoryl chloride at 1900—2000 Å seems to be due to a forbidden ($n \longrightarrow \pi^*$) transition from a non-bonding orbital of the oxygen atom to the antibonding (π^*) molecular orbital of the P–O bond. If this interpretation is correct, the ($n \longrightarrow \pi^*$) transition in phosphoryl compounds is shifted to shorter wavelengths than for carbonyl derivatives, for which the band at about 2800 Å has been ascribed to the ($n \longrightarrow \pi^*$) transition.[13] Thus, for the analogous carbonyl compound, phosgene, the longest-wavelength absorption band occurs at 3050 Å, and continuous absorption starts at 1050 Å, corresponding to an ionisation potential of 11·79 ev.[14] No photoionisation or electron-impact studies of phosphoryl chloride have been reported. The blue shift and decrease in absorptivity in passing from phosphorus trichloride to phosphoryl chloride were again observed in the system dialkylphosphine–dialkyl phosphonate.

EXPERIMENTAL

Materials.—Phosphine and the methylphosphines were prepared and purified as previously described.[10] Dimethyl phosphonate (vapour pressure, 1·7 mm. at 23°) was prepared as described for the diethyl ester.[15] Chlorodiethylphosphine, b. p. 129—130°, was prepared as reported earlier[16] (Found: Cl, 28·6. Calc. for $C_4H_{10}ClP$: Cl, 28·5%); its vapour pressure was 4·3 mm. at 10° and 9·2 mm. at 23°. The other compounds (Fluka AG products) were fractionally distilled (vapour pressure given in parentheses), namely: trimethyl phosphite (4 mm. at 0°; 16 mm. at 23°); triethyl phosphite (2·4 mm. at 24°); diethyl phosphonate (1 mm. at 23°); phosphorus trichloride (14 mm. at −21°; 36 mm. at 0°); phosphoryl chloride (6·5 mm. at 0°; 22 mm. at 23°).

High-vacuum techniques were used. The compounds were transferred by expansion into evacuated quartz cells of 1, 2, 10, or 100 mm. optical paths, fitted with stopcocks and conical joints. Gas pressures were measured with a mercury manometer.

Absorption Spectra.—These were measured with a Beckman DU spectrophotometer down to 2000 Å, and with Hilger Uvispec, Cary 14, and Unicam S.P. 500 spectrophotometers down to 1850 Å. For measurements below 2000 Å, the optical system was purged with nitrogen.

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[12] Mason, *Quart. Rev.*, 1961, **15**, 287; Rao, "Ultra-Violet and Visible Spectroscopy," Butterworths Scientific Publns., London, 1961.

[13] Pople and Sidman, *J. Chem. Phys.*, 1957, **27**, 1270.

[14] Henri and Howell, *Proc. Roy. Soc.*, 1930, **128**, *A*, 192; La Paglia and Duncan, *J. Chem. Phys.*, 1961, **34**, 125.

[15] McCombie, Saunders, and Stacey, *J.*, 1945, 380.

[16] Beeby and Mann, *J.*, 1951, 413.