

6. *Electron-impact Studies of Phosphorus Compounds.*

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The ionisation and appearance potentials of a number of simple phosphorus compounds have been measured. The electron-impact results for phosphine, in conjunction with thermochemical data, indicate a likely mechanism for the fragmentation of phosphine by electron bombardment. The ionisation-efficiency curves for two major fragments from electron impact on trimethylphosphine, for $(\text{Me}_2\text{P}\cdot\text{CH}_3)^+$ and $(\text{Me}_2\text{P})^+$, are identical. Both fragments seem thus to be derived from a common intermediate. Extensive decomposition of dimethyl phosphonate occurred even with electrons of relatively low energy.

ELECTRON-IMPACT spectroscopy has been studied for many hydrocarbons, but the only phosphorus compounds which have been investigated are red phosphorus,¹ phosphine,^{2,3} phosphorus trichloride,⁴ and dichlorotrifluorophosphorane.⁵

Mass-spectral data for the fragmentation of the methylphosphines by electron bombardment have been reported.⁶

RESULTS AND DISCUSSION

Phosphine.—The appearance potentials for singly charged ions from phosphine are given in Table I where they are compared with those previously obtained² by the "linear

¹ Carette and Kerwin, *Canad. J. Phys.*, 1961, **39**, 1300.

² (a) Neuert and Clasen, *Z. Naturforsch.*, 1952, **7a**, 410; (b) Saalfeld and Sved, *Inorg. Chem.*, 1963, **2**, 46.

³ Stevenson, *Radiation Res.*, 1959, **10**, 610.

⁴ Kusch, Hustrulid, and Tate, *Phys. Rev.*, 1937, **52**, 840; Sandoval, Moser, and Kiser, *J. Phys. Chem.*, 1963, **67**, 124.

⁵ Kennedy and Payne, *J.*, 1959, 1228.

⁶ (a) "Mass Spectral Data," Amer. Petroleum Inst., Res. Project 44, No. 1219 (1955); (b) Halmann, *J.*, 1962, 3270.

TABLE 1.
Appearance potentials (A) for ion fragments from phosphine.

Ion	m/e	Reference ion	A (ev), linear extrapol.	A (ev), vanishing current	A (ev), lit.	Ref.
PH_3^+	34	Ar^+	10.3 ± 0.5	10.4 ± 0.3	10.0 ± 0.2	3
PH_2^+	33	Ar^+	14.4	14.0 ± 0.2	11.5 ± 0.3	2b
PH^+	32	Ar^+	13.6	13.1 ± 0.2	14.4 ± 0.2	2b
P^+	31	Ar^+	20 ± 1	16.0 ± 1	12.4 ± 0.2	2b
					16.4 ± 0.4	2b
					18.5 ± 0.2	2b
					20.8 ± 0.3	2b
			Linear extrapol.	Square-root plot ⁷		
PH_3^{2+}	17	Kr^{2+}	15.0	15.6		
PH_2^{2+}	16.5	Kr^{2+}	32.7	34.0		
PH^{2+}	16	Kr^{2+}	21.2	25.1		
P^{2+}	15.5	Kr^{2+}	42 ± 2	42 ± 2		

extrapolation" method. The ionisation-efficiency curves for doubly ionised fragments from phosphine are presented in Fig. 1, together with that of the reference ion Kr^{2+} . Results in Table 1 for doubly charged ions are also derived from a plot of the square root

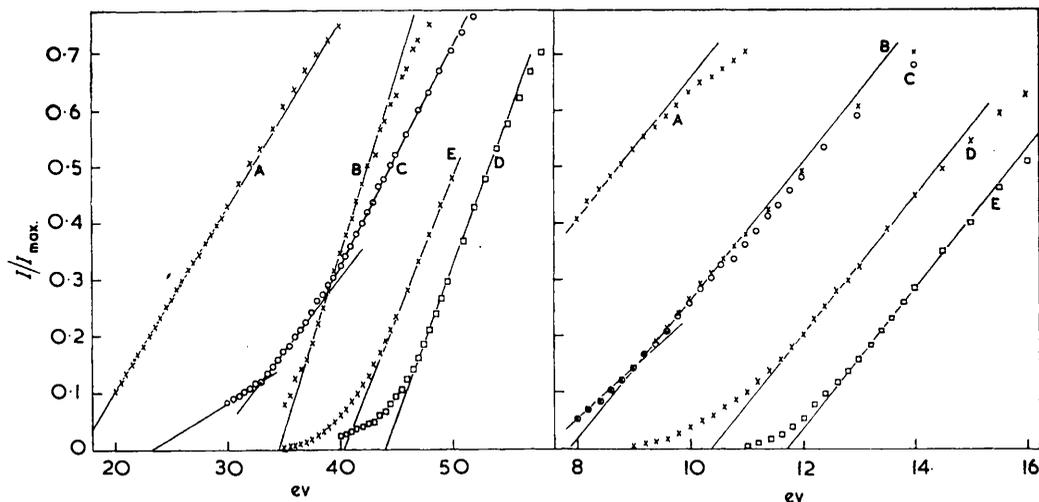


FIG. 1.

FIG. 2.

FIG. 1. Ionisation efficiency curves for doubly ionised fragments PH_3^{2+} (A), PH_2^{2+} (B), PH^{2+} (C), and P^{2+} (D) from phosphine. Reference ion, Kr^{2+} (E). Plot of relative ion current, I/I_{max} , against electron energy (uncorrected).

FIG. 2. Ionisation efficiency curve for Me_3P^+ (A), $\text{Me}_2\text{P}\cdot\text{CH}_2^+$ (B), Me_2P^+ (C), and $(\text{CH}_2)_2\text{P}^+$ (D) from trimethylphosphine. Reference ion, Ar^+ (E).

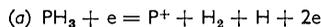
of the ion current against the electron energy.⁷ Neuert and Clasen^{2a} list the value of 16.7 ± 1 ev for the "linear extrapolation" appearance potential of P^+ from phosphine. The ionisation-efficiency curve for P^+ has a very long tail, which may indicate that the ion is formed with appreciable kinetic energy.

The appearance potentials, in conjunction with ionisation potentials from atomic spectroscopy and thermochemical values, can be used for choosing the more probable reaction processes. It has been found that, in many simple cases, the observed appearance potential $A(Z)$ for an ion fragment Z from a molecule RZ is related to its ionisation

⁷ Kiser, *J. Chem. Phys.*, 1962, **36**, 2964.

potential $I(Z)$, and to the energy of dissociation $D(R-Z)$ of the bond^{8,9} by the expression, $A(Z) = I(Z) + D(R-Z)$. This assumes that the dissociation products are formed with little, if any, excitation energy, and that $I(Z) < I(R)$.

The formation of P^+ by electron impact on phosphine may be due to the following process:

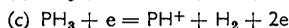
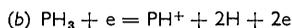


This is thus analogous to the lowest-energy process by which CH_2^+ is formed from methane by electron impact.¹⁰ The lowest appearance potential for P^+ can be predicted by the equation $A(P^+) \geq I(P) + 3\bar{D}(P-H) - D(H-H)$. The ionisation potential of the phosphorus atom has been determined spectroscopically,¹¹ namely $I(P) = 11.0$ ev, while the average energy of dissociation of the P-H bond is known from thermochemical measurements,⁸ $\bar{D}(P-H) = 3.35$ ev. The dissociation energy of the hydrogen molecule is $D(H-H) = 4.48$ ev.¹⁰

Thus $A(P^+) = 11.0 + 3 \times 3.35 - 4.48 = 16.6$ ev.

This predicted value for process (a) is close to the observed value for the "vanishing current" appearance potential of P^+ (see Table 1), and process (a) seems reasonable. The "linear extrapolation" value of 20 ev may be due to a process in which three hydrogen atoms are formed.

The most abundant ion species formed in the usual mass spectrum of phosphine is PH^+ . The most likely mechanisms for its formation may be written:



The fact that the appearance potential of PH^+ is lower than that of PH_2^+ suggests that PH^+ is formed by elimination of a molecule of hydrogen from the parent phosphine. By reaction (b), the appearance potential for PH^+ should be given by:

$$A(\text{PH}^+) \geq I(\text{PH}) + D(\text{PH}_2\text{-H}) + D(\text{PH-H});$$

and by reaction (c) the appearance potential should be lower by the amount of energy of dissociation of the hydrogen molecule, $D(H-H)$. Assuming the dissociation energies $D(\text{PH}_2\text{-H})$ and $D(\text{PH-H})$ to be similar to the average dissociation energy $\bar{D}(P-H)$ in phosphine⁸ (3.35 ev) leads to the following ionisation potential for PH by process (c):

$$I(\text{PH}) \leq A(\text{PH}^+) - \bar{D}(P-H) + D(H-H) = 13.1 - 6.7 + 4.48 = 10.9 \pm 0.5 \text{ ev.}$$

No direct measurement of the photoionisation threshold for the PH radical has yet been reported, although PH is formed readily in the flash photolysis of phosphine.¹²

Doubly Charged Ions from Phosphine.—The following tentative mechanism may account for formation of the doubly charged phosphorus ion, P^{2+} ($m/e = 15.5$):



The appearance potential for this ion should thus be equal to, or larger than, the sum of the potentials for double ionisation of phosphorus, $I(P^I) + I(P^{II})$ and the dissociation energy of phosphine should be given by

$$A(P^{2+}) \geq I(P^I) + I(P^{II}) + 3D(P-H).$$

Inserting the spectroscopic values¹¹ $I(P^I) = 11.0$ and $I(P^{II}) = 19.65$ ev, we obtain a

⁸ Cottrell, "The Strengths of Chemical Bond," 2nd edn., Butterworths Scientific Publns., London, 1958.

⁹ Stevenson, *Discuss. Faraday Soc.*, 1951, **10**, 35.

¹⁰ McDowell and Warren, *Discuss. Faraday Soc.*, 1951, **10**, 53.

¹¹ Moore, "Atomic Energy Levels," Nat. Bureau Standards, Circular No. 467, Washington, D.C., 1952.

¹² Norrish and Oldershaw, *Proc. Roy. Soc.*, 1961, *A*, **262**, 1.

predicted value of $A(\text{P}^{2+}) \geq 40.7$ ev. The close fit to the observed result, 42 ev, seems to support the simple dissociation mechanism (d).

For the formation of the ions PH_2^{2+} and PH_3^{2+} , several mechanisms can be written. Since the potentials for double ionisation of the radicals PH and PH_2 are unknown, no independent check on such mechanisms is available. The very low ionisation potential of 15.6 ev observed for $m/e = 17$ (PH_3^{2+}) is surprising. In the analogous case of NH_3^{2+} , the threshold potential was reported¹³ as 33.7 ± 0.2 ev.

Trimethylphosphine.—The ionisation potential for trimethylphosphine (Table 2).

TABLE 2.

Appearance potentials (vanishing current) for ion fragments from trimethylphosphine. (Reference ion, Ar^+ .)

Ion	$(\text{CH}_3)_3\text{P}^+$	$(\text{CH}_3)_2\text{PCH}_2^+$	$(\text{CH}_3)_2\text{P}^+$	$(\text{CH}_3)_2\text{P}^+$	CH_2P^+	CH_3^+
m/e	76	75	61	59	45	15
A (ev), obs.	9.2 ± 0.5	11.8 ± 0.2	11.8 ± 0.2	15 ± 1	17 ± 1	21.7 ± 0.5

$I[(\text{CH}_3)_3\text{P}] = 9.0 \pm 0.5$ ev, indicates that the threshold for photoionisation should be at 1370 ± 100 Å. No vacuum-ultraviolet absorption measurement has yet been reported for this molecule.

The most remarkable result of electron impact on trimethylphosphine is the identity in the ionisation-efficiency curve for the ion fragments $(\text{CH}_3)_2\text{P}\cdot\text{CH}_2^+$ and $(\text{CH}_3)_2\text{P}^+$ (see Fig. 2). This might be understood if we assume a mechanism in which both fragments are formed rapidly (in less than 10^{-5} sec., the time required for leaving the ion source) from a common intermediate, probably an excited state of $(\text{CH}_3)_3\text{P}^+$.

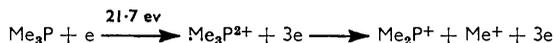
It is possible to use the observed appearance potential of 11.8 ± 0.2 ev for these ions, in conjunction with the mean dissociation energy $\bar{D}(\text{P-C}) = 2.73$ ev for the P-C bond in trimethylphosphine (from thermochemical measurements¹⁴) in order to derive an upper value for the ionisation potential for the $(\text{CH}_3)_2\text{P}^+$ ion formed by the reaction:



In this case the equation $A[(\text{CH}_3)_2\text{P}^+] = I[(\text{CH}_3)_2\text{P}] + D[(\text{CH}_3)_2\text{P}-\text{CH}_3]$ should be valid, because the ionisation potential of the methyl radical, $I(\text{CH}_3) = 9.9$ ev,¹⁴ must be more than $I[(\text{CH}_3)_2\text{P}]$. Inserting the above value of $\bar{D}(\text{P-C})$, one gets:

$$I[(\text{CH}_3)_2\text{P}] \leq 11.8 - 2.73 = 9.1 \pm 0.2 \text{ ev.}$$

The formation of the $m/e = 15$ peak of CH_3^+ can be accounted for by the following scheme, which may involve the doubly charged trimethylphosphine ion-molecule as an intermediate:



The appearance potential of the methyl ion should be larger than that of the Me_2P^+ ion by the potential of ionisation of the methyl radical $I(\text{Me}) = 9.9$ ev,¹⁴ so that we have:

$$A(\text{Me}^+) \geq I(\text{Me}) + I(\text{Me}_2\text{P}) + D(\text{Me}_2\text{P}-\text{Me}) = I(\text{Me}) + A(\text{Me}_2\text{P}^+) = 9.9 + 11.8 = 21.7 \text{ ev.}$$

This calculated value is the same as the directly observed value (see Table 2), $A(\text{Me}^+) = 21.7 \pm 0.5$ ev. If the above mechanism is right it can be concluded that the methyl ion is formed without appreciable kinetic or excitational energy. The ionisation efficiency curve of Me_2P^+ should show a slight upward peak at 21 ev, which would be difficult to detect in the presence of a high abundance of Me_2P^+ from the ejection of methyl radicals.

Dimethylphosphine.—The ionisation and appearance potentials for the most abundant

¹³ Dorfman and Morrison, *J. Chem. Phys.*, 1961, **35**, 575.

¹⁴ Field and Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, New York, 1957, p. 299.

TABLE 3.

Appearance potentials (linear extrapolation) for ion fragments from dimethylphosphine. (Reference ion, Ar⁺.)

Ion	(CH ₃) ₂ PH ⁺	(CH ₃) ₂ P ⁺	CH ₃ P ⁺	HCP ⁺	P ⁺
<i>m/e</i>	62	61	46	44	31
<i>A</i> (ev)	9.7	12.2	11.9	14.1	11.9

positive ions from dimethylphosphine are given in Table 3. The ion of *m/e* = 61 (Me₂P⁺) is presumably the same as that produced by electron impact on trimethylphosphine. Its formation may be described by the equation, Me₂PH + e = Me₂P⁺ + H + 2e. Here the relation $A[(\text{Me}_2\text{P})^+] \geq I(\text{Me}_2\text{P}) + D(\text{Me}_2\text{P}-\text{H})$ should be valid, because the ionisation potential of the hydrogen atom,¹¹ $I(\text{H}) = 13.595$ ev, must be greater than $I(\text{Me}_2\text{P})$. Inserting, as an approximate value of the dissociation energy of the P-H bond in dimethylphosphine, its average value in phosphine,⁸ $\bar{D}(\text{P}-\text{H}) = 3.3$ ev, one gets $I(\text{Me}_2\text{P}) \leq 12.2 - 3.3 = 8.9$ ev, a value similar to that obtained above for the Me₂P radical formed by electron impact on trimethylphosphine.

Dimethyl Phosphonate.—The mass spectrum of dimethylphosphonate has been described before.¹⁵ Appearance potentials, as well as relative abundances for the major fragments (at 20 ev ionisation potential) are given in Table 4. Even quite extensive rupture of the molecule, such as that producing the very highly abundant ions HPO₃⁺ and PO₃⁺, occurs with relatively low appearance potentials, namely, 11.2 and 13.5 ± 0.5 ev.

The ion HPO₃⁺ may possibly be produced by the process (CH₃O)₂PHO + e = HPO₃⁺ + C₂H₆ + 2e, which involves elimination of an ethane molecule. Assuming the dissociation

TABLE 4.

Appearance potentials (linear extrapolation) for ion fragments from dimethyl phosphonate. (Reference ion, Ar⁺.)

<i>m/e</i>	110	109	95	80	79	47
Tentative assignment	(MeO) ₂ PHO ⁺	(MeO) ₂ PO ⁺	(MeO)PHO ₂ ⁺	HPO ₃ ⁺	PO ₃ ⁺	PO ⁺
<i>A</i> (ev)	10.5	12.7	11.9	11.2	13.5	16.3
Relative abundance at 20 ev	5.9	7.3	14.3	100	95	16.7

energy of the methyl-oxygen bond in dimethyl phosphonate to be similar to that of the H₃C-OH bond in methanol⁸ (3.91 ev), and taking the bond dissociation energy in ethane $D(\text{CH}_3-\text{CH}_3) = 3.65$ ev, we obtain $A(\text{HPO}_3^+) \geq I(\text{HPO}_3) + 2D(\text{CH}_3-\text{OH}) - D(\text{CH}_3-\text{CH}_3)$. An upper estimate for the ionisation potential of the HPO₃ radical by the above mechanism is thus $I(\text{HPO}_3) \leq 11.2 - 2 \times 3.9 + 3.65 = 7.0$ ev.

EXPERIMENTAL

The mass-spectrometer used for appearance-potential measurements was type MS-2 of Associated Electrical Industries. The ionising electron beam is controlled by an electronic regulator which senses the trap current and keeps it constant by varying the filament current. The accelerating voltage of the electrons, measured with the voltmeter, is the voltage between the filament and the cage.

The electronic regulator is built so that the electron-accelerating voltage can be varied continuously in two ranges: from 8 to 20 v with a trap current of 15/μA, and from 20 to 80 v with a trap current of 100/μA. Working beyond these ranges, or in the high-voltage range with low trap current, or in the low-voltage range with high trap current, causes instability of the ion source. Thus we had to restrict our experiments to one of these two ranges and could not pass continuously during appearance-potential measurements from one range to the other.

¹⁵ Long and Sackman, *Trans. Faraday Soc.*, 1957, **58**, 1606.

Phosphine and the methylphosphines were prepared and purified as described.¹⁶

Argon and krypton (Matheson Co.) were used without purification.

Appearance potentials of the various ion fragments were determined for mixtures of the vapour of the phosphorus compound with either argon or krypton as internal reference. The first and second ionisation potentials of the rare gases were taken from spectroscopic measurements¹¹ to be: $\text{Ar}^+ = 15.76$, $\text{Ar}^{2+} = 43.38$, $\text{Kr}^+ = 14.00$, and $\text{Kr}^{2+} = 38.56$ ev. Either the linear-extrapolation or the vanishing-current¹⁷ method of deducing the appearance potential of an ion from its ionisation efficiency curve was applied.

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¹⁶ Halmann, "Chemical Effects of Nuclear Transformations," Internat. Atomic Energy Agency, Vienna, 1961, Vol. I, p. 195.

¹⁷ Lossing, Tickner, and Bryce, *J. Chem. Phys.*, 1951, **19**, 1254.
