

The Phosphorus-Phosphorus Bond: some Electron Impact Studies

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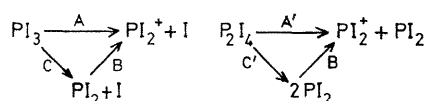
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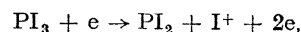
PHYSICAL data concerning the P-P bond, even in very simple systems, are scarce. From some detailed mass spectroscopic studies of both phosphorus tri-iodide and diphosphorus tetraiodide,¹ an estimate of the strength of the P-P bond may be made. Relevant results are shown in the cycles:



The appearance potentials for processes A and A', are 11.9 ± 0.15 and 12.8 ± 0.15 eV respectively. If the literature² value for the energy of the dissociation process C, $184.1 \text{ kJ mole}^{-1}$ (44 kcal. mole⁻¹), is adopted, then the bond dissociation energy $D(\text{PI}_2-\text{PI}_2)$ (process C') is $271.0 \text{ kJ mole}^{-1}$ (64.8 kcal. mole⁻¹). This is in excellent agreement with a previous estimate,³ $269.9 \text{ kJ mole}^{-1}$ (64.5 kcal. mole⁻¹) and also with two values, 263.6 and $217.6 \text{ kJ mole}^{-1}$ (63 and 52 kcal. mole⁻¹) derived from a mass spectroscopic study⁴ of PCl_3 and P_2Cl_4 for $D(\text{PCl}_2-\text{PCl}_2)$. Cracking patterns for the chloride⁴ and iodide¹ systems differ considerably and in the former the appearance potential of PCl_2^+ from PCl_3 exceeds that of the appearance potential of PCl_2^+ from P_2Cl_4 , in contrast to the above results (processes A, A').

In both chloride and iodide systems the value corresponding to process C was estimated as one third of the heat

of formation of PI_2^+ in respect to the gaseous elements *i.e.* with the implicit assumption that $D(\text{PX}_2-\text{X}) = \bar{D}(\text{P}-\text{X})$. This is known to be invalid for other Group V molecules, *e.g.* NF_3 , NH_3 ; hence a third experimental result of this investigation, a value of 12.7 ± 0.15 eV for the appearance potential of I^+ from PI_3 is relevant. On the assumption that this results from the process



use of the value⁵ of 10.45 eV for the ionisation potential of iodine, gives $D(\text{PI}_2-\text{I}) = 217 \text{ kJ. mole}^{-1}$ (52 kcal. mole⁻¹) and $D(\text{PI}_2-\text{PI}_2) = 309 \text{ kJ. mole}^{-1}$ (73 kcal. mole⁻¹).

Since all values for the phosphorus-iodine bond strengths have previously relied on assumed values of $\Delta H^\circ_{\text{vap}} \text{PI}_3$ or P_2I_4 , the latter values are entirely reasonable. Hence they may now be used to estimate the heats of sublimation. Direct determination of these is extremely difficult, owing to the very low vapour pressures at ambient temperatures and thermal instability at elevated temperatures. However, experimental studies, with Knudsen-type and thermal conductivity gauges are in progress.

Appearance potential measurements were performed by use of an AEI model MS2H mass spectrometer with a direct inlet system for solid samples of PI_3 and P_2I_4 ; the method of Lossing *et al.*⁶ was used, with argon as internal standard.

(Received, February 13th, 1969; Com. 198.)

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