Exploring why is PF₅ a stable molecule but not PH₅.

Covalent compounds that exceed the “octet rule” by having more than four pairs of electrons around a central atom are commonly known as “hypervalent” molecules. Your textbook explains that stable hypervalent molecules can be formed when the central atom is in the $n = 3$ row or higher because $d$-orbitals are available to form the extra bonds. While this successfully explains why hypervalency is not observed in the $n = 2$ row (there are no $2d$ orbitals), it does not address why PF₅ is stable but PH₅, on the other hand, is never observed in nature.

Part I
Using average bond energies from your textbook (Table 9-2), calculate the energy change for the following reactions:

- $\text{PF}_3(g) + \text{F}_2(g) \rightarrow \text{PF}_5(g)$
- $\text{PH}_3(g) + \text{H}_2(g) \rightarrow \text{PH}_5(g)$

Based on your calculations, do you expect PF₅ to be energetically stable relative to PF₃ and F₂? What about PH₅ relative to PH₃ and H₂?

Part II
An alternative view is that stable hypervalent molecules have only four covalent bonds. Any “extra” bonds are ionic in character with the extra electrons assigned to the outer atoms. In this case, they do not exceed the octet rule. With this model we can draw a series of resonance structures as shown below for PF₅. Thus, PF₅ has net four covalent bonds and one ionic bond. (In this picture, the dashed line represents the “ionic” bond.)

Since we are attempting to predict a priori if PF₅ is stable, we will make the argument based only on information from PF₃, F₂, P and F.

To form PF₅ from PF₃ and F₂, we will have to:
(a) break the F–F bond
(b) form two new P–F bonds
(c) change the ionic character of the P–F bonds by ensuring that a net +1 charge is moved off P and distributed on the outer F atoms.

In the following steps, convert all energies to kcal/mol using the conversion factors below.

Energy Conversion factors
- 1 a.u. (or hartree) = 627.51 kcal/mol.
- Coulomb’s Law: if the charges are in atomic units and the distance is in Angstroms, the conversion factor is $k = 331.31$ for energy in kcal/mol.
- 1 eV = 23.06 kcal/mol.
Step 1: Build and calculate the P atom, F atom, F₂ molecule and the PF₃ molecule.

(a) Calculate the bond energy in three P–F bonds of PF₃ using PF₃ → P + 3 F. Do this by subtracting the calculated energy of PF₃ from the energies of one P and 3 F atoms.

(b) Calculate the bond energy of a single P–F bond in PF₃.

(c) What is the P–F bond distance in Angstroms?

(d) What are the ESP atomic charges on P and F in atomic units?

(e) Assuming that the ionic character of the bond can be described by Coulomb’s Law, calculate the ionic contribution to the P–F bond energy using \[ E = \frac{(kq_Pq_F)}{r} \], where \( q_P \) and \( q_F \) are the atomic charges on P and F respectively and \( r \) is the P–F bond distance.

(f) Assuming that the P–F bond energy has only ionic and covalent contributions, calculate the covalent contribution from your results in Steps 1(b) and 1(e).

(g) Calculate the F–F bond energy in kcal/mol using F₂ → 2 F. Do this by subtracting the calculated energy of F₂ from the energies of 2 F atoms.

Step 2: Calculate the cost of moving charge from P to F.

(a) Look up the ionization potential of PF₃ and the electron affinity of F at the NIST Chemistry WebBook (http://webbook.nist.gov/chemistry/).

(b) According to our model, PF₅ ends up with a net +1 atomic unit charge on P. Based on the atomic charge on P in PF₃, how much additional charge (in atomic units) needs to be moved off the P in PF₃? [Hint: refer to Step 1(d).]

(c) Assuming that the cost of moving this charge in Step 2(b) is a percentage of the full ionization potential of PF₅, calculate the cost of moving the charge. [The full ionization potential from Step 2(a) is assumed to be the cost of moving 1.000 units of charge from P in PF₅.]

(d) Assuming that the gain in energy for moving this charge in Step 2(b) is a percentage of the full electron affinity of F, calculate the gain for moving the charge.

Step 3: Recalculate the value of the P–F bonds.

(a) Assuming the same bond lengths in PF₅ and PF₃, calculate the ionic contribution for the five partial ionic bonds in PF₅. (Note that the charges on P and F are now +1 and −0.2 respectively). [This leads to a net of one ionic bond.]

(b) Assuming that PF₅ has net four covalent bonds, and the covalent contribution of the P–F bond is the same in PF₅ and PF₃ [see Step 1(f)], calculate the total covalent contribution of four bonds.
Step 4: Put everything together.

Energy costs:

Step 1(a): Three old P–F bonds in PF₃.

Step 1(g): Breaking the F–F bond in F₂.

Step 2(c): Moving charge away from P in PF₃.

Energy gains:

Step 2(d): Moving charge to outer F atoms.

Step 3(a): Five partial ionic P–F bonds in PF₅.

Step 3(b): Four covalent P–F bonds in PF₅.

Does the gain outweigh the cost (or vice versa)?

Is PF₅ stable with respect to PF₃ and F₂?

Step 5: Repeat Steps 1-4 to find out if PH₅ is stable compared to PH₃ + H₂.

Energy costs:

Step 1(a): Three old P–H bonds in PH₃.

Step 1(g): Breaking the H–H bond in H₂.

Step 2(c): Moving charge away from P in PH₃.

Energy gains:

Step 2(d): Moving charge to outer H atoms.

Step 3(a): Five partial ionic P–H bonds in PH₅.

Step 3(b): Four covalent P–H bonds in PH₅.

Does the gain outweigh the cost (or vice versa)?

Is PH₅ stable with respect to PH₃ and H₂?