Summary of Nitrogen Group (Group VA) Trends:

1. The hydrides become less thermally stable and more reactive down the column. The M-H and M-CH3 mean bond enthalpies decrease in strength down the group and consequently the hydrides and alkyls become less stable.

2. The majority of nitrogen compounds are covalent. The main exceptions being those based on the nitride ion.

3. Multiple bond formation:
   • Nitrogen forms very strong multiple \( \pi-\pi \) bonds to itself and neighboring elements belonging to the same row, e.g. \( \text{CN}^-, \text{N}_2, \text{NO}^+ \). Compounds of P, As, and Bi with multiple bonds may be obtained if large groups are introduced into the molecules, e.g. \( \text{P}_2\text{R}_2 \) and \( \text{As}_2\text{R}_2 \). Similar multiply bonded compounds of Sb are not known.

4. Coordination numbers:
   • The coordination numbers increase down the group. For nitrogen 3 and 4 coordination predominate. Phosphorous and arsenic in addition form octahedral complexes and higher coordination numbers are observed for Sb and Bi.

5. Increased metallic character
   • The elements become increasingly metallic down the column in their chemical and physical properties. Down the group the oxo cations, e.g. \( \text{SbO}^+ \) and \( \text{BiO}^+ \) become more prevalent.

6. The oxides become more basic down the column.
   • Phosphorous and arsenic oxides are acidic, antimony oxide is amphoteric, and that of bismuth is basic.

7. The halides become more ionic and increasingly adopt infinite structures in preference to molecular ones.

8. Catenation occurs in the order: \( \text{N} < \text{P} > \text{As} > \text{Sb} > \text{Bi} \). Phosphorous forms a wide range of ring and cage compounds because of the favorable P-P bond enthalpy.

9. Negative oxidation states:
   • For nitrogen the \( \text{N}^{3-} \) ion is well established in the ionic nitrides of the electropositive elements. The anionic derivatives of the heavier elements frequently retain element-element bonds, e.g. \( \text{Sb}_4^{2-}, \text{Bi}_4^{2-}, \text{Sb}_{7}^{3-} \), and \( \text{As}_{11}^{3-} \).

10. The donor/acceptor behavior of R3M:
   • Donor/Lewis base ability: \( \text{N} < \text{P} > \text{As} > \text{Sb} > \text{Bi} \)
   • Steric effects: \( \text{N} > \text{P} \sim \text{As} > \text{Sb} > \text{Bi} \) and increase with bulk of substituents: \( \text{PR}_3 > \text{PR}_2\text{H} > \text{PRH}_2 > \text{PH}_3 \)
   • \( \pi \)-acidity (see lecture): \( \text{R}_3\text{P} > \text{R}_3\text{As} > \text{R}_3\text{Sb} > \text{R}_3\text{Bi} \)
   • Lewis acidity of the +5 fluorides: \( \text{PF}_5 > \text{AsF}_5 > \text{SbF}_5 \)

11. Hydrolysis of halides:
   • In the +5 oxidation state \( \text{PF}_5 \) is not readily hydrolyzed, \( \text{AsF}_5 \) hydrolyses, \( \text{SbF}_5 \) vigorously reacts with water. \( \text{BiF}_5 \)
reacts explosively with water. In the +3 oxidation state NF$_3$ is unreactive, PF$_3$ reacts only with OH$^-$ not OH$_2$, AsF$_3$, SbF$_3$ are soluble in water, BiF$_3$ is insoluble in water but soluble in inorganic acids.

12. **Stabilization of the +3 oxidation state relative to +5 oxidation state.** The trend is less well defined than that of group IVa and in fact an alternation in stabilities is observed. This may be illustrated by the following halide stabilities:

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>P</th>
<th>As</th>
<th>Sb</th>
<th>Bi</th>
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<tbody>
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<td>stable</td>
<td>stable</td>
<td>stable</td>
</tr>
<tr>
<td>ECl$_5$</td>
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<td>known but unstable</td>
<td>stable</td>
<td>unknown</td>
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<tr>
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<tr>
<td>EBr$_3$</td>
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<tr>
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<td>known but unstable</td>
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</tr>
</tbody>
</table>

- The +5 oxidation state halides are unknown for N, well defined for P, only stable for As as fluoride, well defined for the fluoride and chloride of antimony, and only known for the fluoride for Bi.
- For both oxidation states the stability order is F > Cl > Br > I as anticipated by the ordering of the mean enthalpies, i.e., fluoride forms the strongest bonds and iodine the weakest.
- The oxides show a similar trend. Bi$^{V}$ and N$^{V}$ oxides and oxoacids are strongly oxidizing whereas P$^{V}$ oxides and oxoacids are very stable and As$^{V}$ and Sb$^{V}$ oxides and oxoacids are mildly oxidizing.

Contributors

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