**Elements of the 4p Row in their Group Maximum Oxidation State**

***Introduction***

In Chapter 4, Section 4.2 on pages 62-63, there is a short section which considers the observed reluctance of elements of the 4p row to exhibit their group maximum oxidation state in the compounds which they form. Specifically, these are compounds of Ga(III), Ge(IV), As(V), Se(VI) and Br(VII) although this reluctance is only really apparent for As(V), Se(VI) and Br(VII). Krypton has such a limited chemistry that we need consider it no further; in none of its known compounds is it found in an oxidation state greater than Kr(II), e.g. KrF2.

The reason generally offered to explain this observation is that the presence of the preceding 3d row elements with their poorly shielding 3d electrons leads to the 4p elements having a greater effective nuclear charge (Z\*) which inhibits their ability to employ all of their valence electrons in bonding. We encountered other properties of certain 4p elements where the effect of the 3d row was evident, for example, the greater electronegativity of Ga *vs* Al. In this addendum, we will expand a little on the explanation and present a number of examples which illustrate the effect. However, before doing so, we should briefly consider oxidation state and valence for the compounds we’ll encounter. Recall that in Section 4.1 in Chapter 4 we described oxidation state and valence in some detail and made the point that these two terms have quite different definitions. Nevertheless, in all of the compounds we’ll consider here, the elements to which the 4p element is bonded have a greater electronegativity so, for example, a pentavalent arsenic compound is also a compound of As(V). We can therefore use the terms interchangeably in this instance and we make this point since some texts talk about As(V) compounds whilst others refer to the same compounds as pentavalent arsenic. We may therefore expand on the title and consider compounds of elements of the 4p row in their group maximum oxidation state or group maximum valence.

It was Dasent1 who was one of the first to draw attention to the topic under discussion and his explanation considered certain differences in ionisation energies for the respective elements. Thus, the data presented in Figure 1 shows the differences between the 5th and 6th ionisation energies for Cl, Br and I, the differences between the 4th and 5th ionisation energies for S, Se and Te and the differences between the 3rd and 4th ionisation energies for P, As and Sb which each reflect the difference between the processes s2p1  s2 and s2  s1, i.e. breaking into the s2 pair. It is clear from Figure 1 that in the case of As, this value is the highest in the triad of P, As and Sb and that whilst this is not the case for Se and Br in their respective triads, the values are clearly greater than a value midway between the elements on either side in their groups.



**Figure 1**. The differences between the 5th and 6th ionisation energies for Cl, Br and I, the differences between the 4th and 5th ionisation energies for S, Se and Te and the differences between the 3rd and 4th ionisation energies for P, As and Sb all in kJ mol–1. Values for the ionisation energies used to construct Figure 1 are taken from Emsley.2

It is important to state that we are not forming As5+, Se6+ or Br7+ cations in any of the compounds we are about to consider. They are all covalent species and when we talk about a compound of As(V) we are employing a formal oxidation state and there is no suggestion that the compound is ionic and contains an As5+ cation. Nevertheless, these ionisation energy data provide us with an insight into how strongly the valence electrons are held and, in particular, effect of the higher Z\* value for the 4p elements.

What follows below are some examples of compounds which are known for As(V), Se(VI) and Br(VII) and comparisons with the lighter and heavier members of their respective groups to illustrate their reduced stability. References are given to original sources where appropriate. Otherwise, the examples chosen and the associated thermodynamic data are taken from the general texts listed in the bibliography in the book.

***Arsenic(V) or pentavalent arsenic***

On page 109 in Chapter 6, we noted two compounds of As(V), namely AsCl5 and [AsCl5(OPMe3)]. In the case of the former, we stated that whilst PCl5 and SbCl5 are stable at room temperature, AsCl5 decomposes above –50˚C to AsCl3 and Cl2. This is one of the most pertinent examples of the effect described in this addendum. We also noted, however, that despite the thermal instability of AsCl5, the acid-base complex [AsCl5(OPMe3)], in which the Lewis acidic AsCl5 is complexed by the ligand trimethylphosphine oxide, is stable up to +50˚C and furthermore, that there are many examples where an apparently unstable oxidation state can be stabilised by complexation with Lewis bases. This suggests that the thermal instability of AsCl5 may be kinetic as well as thermodynamic in origin and can be arrested by effectively saturating the coordination sphere of the central element. We noted also a further, more general, observation: it is often observed that for higher oxidation states where a neutral compound is unstable, the related anions are rather more stable. This is the case in the present example in that compounds containing the [AsCl6]– anion are generally stable at room temperature. An explanation sometimes offered in the example of anions is that the negative charge raises the energy of, in this case, the Cl s orbitals which leads to better overlap with the central element centre and stronger bonds result.

It is also worth noting that thermally stable compounds containing the [AsCl4]+ cation are known along with a range of organo-arsonium cations [AsR4]+. Moreover, neutral organo-arsenic(V) compounds such as AsPh5 are reasonably stable. An explanation for the instability of AsCl5 *vs* AsPh5 most likely has much in common with the explanation offered for the instability of PbCl4 *vs* the much more stable PbEt4 given on pages 71-72 in Chapter 4.

Two other examples of As(V) compounds are worth highlighting here. In terms of thermal stability, POCl3 is stable at room temperature whereas AsOCl3 decomposes above 0˚C. However, we can also consider the stability of oxidation states in terms of electrochemical data as we did for the heavier Group 13 elements Ga, In and Tl in Chapter 4 in relation to the inert pair effect. Thus, in this context, the arsenate anion [AsO4]3– is observed to be much more oxidising than the corresponding phosphate anion [PO4]3– as is evident from the standard reduction potentials shown in Eqns. (1) and (2), the more positive the potential, the more easily the species in question is reduced to a lower oxidation state, i.e. the better it is as an oxidising agent.3 Indeed, H3PO4 is not an oxidising agent under normal conditions.

H3AsO4 + 2H+ + 2e– ⇌ H3AsO3 + H2O *E*o = +0.560 V (1)

 H3PO4 + 2H+ + 2e– ⇌ H3PO3 + H2O *E*o = –0.276 V (2)

***Selenium(VI) or hexavalent selenium***

With regard to Se(VI) chemistry, it is illuminating to consider the standard enthalpies of formation of the trioxides and the dioxides. These data are collected in Table 1 below which clearly demonstrate the relative instability of SeO3 compared with either SO3 or TeO3 which is also evident from the exothermic nature of the reaction shown in Eqn. (3) using the values for selenium derived from Table 1. Furthermore, the selenate anion, [SeO4]2–, is more strongly oxidising than sulfate, [SO4]2–, and is also thermally less stable and evolves oxygen when heated above about 200˚C.

**Table 1**. The standard enthalpies of formation (D*H*fo) in kJ mol–1 for the di- and trioxides of S, Se and Te.

|  |  |  |  |
| --- | --- | --- | --- |
| SO2 | –297 | SO3 | –432 |
| SeO2 | –230 | SeO3 | –184 |
| TeO2 | –325 | TeO3 | –348 |

SeO3  SeO2 + ½ O2 D*H*ro = –46 kJ mol–1 (3)

Similarly, with the hexafluorides. SF6, SeF6 and TeF6 are all known compounds but the standard enthalpies of formation (D*H*fo) in kJ mol–1 for each are –1210, –1117 and –1320, the lowest value being for selenium.

***Bromine(VII) or heptavalent bromine***

Besides the [BrF6]+ cation, the only examples of Br(VII) compounds are the perbromate ion [BrO4]– and the protonated derivative, perbromic acid, HBrO4. In fact, the perbromate ion was not synthesised until 1968 and its synthesis requires the use of very strong oxidising agents such as F2 or XeF2 as shown in Eqns. (4) and (5), although once prepared, perbromate is kinetically stable in aqueous solution.

Na[BrO3] + F2 + 2 NaOH  Na[BrO4] + 2 NaF + H2O (4)

 Na[BrO3] + XeF2 + H2O  Na[BrO4] + 2 HF + Xe (5)

That perbromate is a stronger oxidising agent than either perchlorate or periodate is clear from the standard reduction potentials shown in Eqns. (6)-(8).

[ClO4]– + 2H+ + 2e– ⇌ [ClO3]– + H2O *E*o = +1.201 V (6)

[BrO4]– + 2H+ + 2e– ⇌ [BrO3]– + H2O *E*o = +1.85 V (7)

 H5IO6 + H+ + 2e– ⇌ [IO3]– + 3H2O *E*o = +1.60 V (8)

Moreover, the corresponding standard enthalpies of formation (D*H*fo) in kJ mol–1 for the potassium salts of perchlorate, perbromate and periodate are: K[ClO4], –432; K[BrO4], –288; K[IO4], –461. The substantially lower value for K[BrO4] compared to potassium perchlorate and periodate is notable.

***Conclusions***

The examples and data presented above for a selection of halides, oxides and oxoanions of As(V), Se(VI) and Br(VII) all reveal a thermodynamic instability inherent in these particular oxidation states. Compounds in oxidation states with a value of two less, i.e. As(III), Se(IV) and Br(V), are much more common and more thermodynamically stable but although it might be tempting to do so, we should not describe this effect as an ‘inert pair effect’. This term is more properly associated with elements of the 6p row, e.g. Tl, Pb and Bi, as discussed in detail in Chapter 4 although we should recognise that the origins of the more stable lower oxidation states encountered in the chemistry of the 4p and 6p elements have much in common.

Finally, as we noted on page 63 in Chapter 4, the feature of the 4p elements described here (in terms of the stability of certain oxidation states) along with the, somewhat similar, inert pair effect for the 6p elements is sometimes referred to as the alternation effect. Thus, in Group 15, for example, compounds of P(V) and Sb(V) are not especially oxidising whereas those of N(V), As(V) and Bi(V) certainly are. A question often asked is that whilst the effect of the poorly shielding 3d electrons on the 4p electrons is clear, is it not the case that a similar effect would be expected for the 5p elements as a consequence of the 4d electrons? The answer is yes, but as ionisation energies generally decrease down a group (see Figure 1), the effect is most marked for the 4p row. In the case of the 6p elements, these are now preceded by the first of the f-rows (4f) which accounts (in part) for the inert pair effect (described in more detail in Chapter 4) and it is on this basis that we can appreciate the origins of the alternation effect.

***References***

1. *Non-Existent Compounds*, Dasent, W. E., *J. Chem. Ed*., 1963, 40, 130-134.
2. Emsley, J. (1989). *The Elements*, Oxford University Press.
3. Reduction potentials can vary slightly according to the source. The values quoted in Eqns. (1), (2) and (6)-(8) are taken from Miessler, G. L., Tarr, D. A. (2004). *Inorganic Chemistry* (3rd edn), Pearson.