## Stability of Zerovalent Compounds in the Nickel Triad. Interplay of Ionization Potential and Electron Affinity

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It is well known that the zerovalent compounds of the nickel triad follow the stability order Ni > Pt > Pd where the compound containing the 4th row element is less stable than those containing either the 3rd or the 5th row element. Several types of evidence point to this effect. The decomposition temperatures of the $M(PF_3)_4$ compounds have been reported as follows:[1] Ni, > 155°; Pd, > –20°; Pt, > 90 °C. Kinetic data[2] for substitution reactions of $M[P(OC_2H_5)_3]_4$ have given enthalpy of activation values which follow the order Ni ≈ Pt > Pd. More recently, force constants for the metal–carbon bonds in $M(CO)_4$ have been obtained:[3] Ni, 1.80; Pd, 0.82; Pt, 1.28 mdyn/Å. The metal–nitrogen force constants in the mono(dinitrogen) compounds $MN_2$ follow the same trend:[4] Ni, 2.51; Pd, 1.89; Pt, 2.27 mdyn/Å. The purpose of this correspondence is to point out that the trend[5] in force constants and decomposition temperature (Ni > Pt > Pd) is paralleled by the trend in the function (EA – IP), where EA refers to the *electron affinity* and IP the *ionization potential* of the metal in its $d^{10}$ valence state.

The usual bonding description for these zerovalent compounds involves the metal in its $d^{10}$ valence state wherein the metal accepts a pair of electrons into an empty valence *s* or *p* orbital in forming the σ bond. In order to decrease the build-up of negative charge on the metal, there is also π back bonding from the metal $d^{10}$ system into low-lying π* or empty $d_\pi$ orbitals on the ligand. The ability of a metal to form a strong σ bond should be related to the EA of the free metal atom; the *larger* the EA the *stronger* the σ bond will be. On the other hand, π back bonding should be related to the $d^{10} \rightarrow d^9$ IP of the free metal atom; the *smaller* the IP the *stronger* the π back bonding will be. The importance of considering both EA and IP was recognized by Nyholm in 1961[6] although the function (EA – IP) was never explicitly employed.

In the Table we present the values of EA and IP for Ni, Pd, and Pt which were derived by Nyholm for the $d^{10}$ valence state.[6] Also given is the difference,

TABLE. Ionization Potentials (IP) and Electron Affinities (EA) for Nickel, Palladium, and Platinum.[a]

| Metal | IP (eV) $d^{10} \rightarrow d^9$ | EA (eV) $d^{10}s^1 \rightarrow d^{10}$ | (EA – IP) (eV) |
|---|---|---|---|
| Ni | 5.81 | 1.2 | –4.6 |
| Pd | 8.33 | 1.3 | –7.0 |
| Pt | 8.20 | 2.4 | –5.8 |

[a] Reference 6.

EA – IP. It is seen that the trend in (EA – IP) is paralleled by that observed for the force constants and decomposition temperatures mentioned above: Ni > Pt > Pd.

The bonding trends in the nickel triad can be summed up as follows. The σ bond strength is related to the trend in EA, Pt > Pd ≈ Ni. The π back bonding strength varies with –IP and is Ni > Pt ≈ Pd. Hence, Ni is a strong π bonder, Pt is a strong σ bonder, but Pd is relatively weak in both.

Other transition metal triads often exhibit the same trend as that shown in the nickel triad, namely, that the compound containing the 4th row element is less stable than those containing either the 3rd or 5th row element.[7,8] To provide just one example in the chromium triad, the M–CO force constants[9] and bond dissociation energies[8,10,11] for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ show that the Mo compound has the weakest M–CO bond strength. In the following paragraphs we show that it is unlikely that the trend in (EA – IP) and stability is fortuitous in the nickel triad. In fact, the same function (EA – IP) is probably responsible for the relative instability of the 4th row element for zerovalent compounds in all of the triads.

The major criticism of the function (EA – IP) is that the electron affinities are estimated values. For the nickel triad, Nyholm obtained EA by extrapolating a plot of √IP through an isoelectronic sequence (e.g., $Ni^-$, $Cu^0$, $Zn^{+1}$, $Ga^{+2}$).[6] These plots resulted in the values presented in the Table for the process $d^{10}s^1 \rightarrow d^{10}$ and indicate that the EA of Pt is about 1 eV greater than that for Ni and Pd. There are several pieces of evidence which indicate that this trend in EA is correct. (i) Another method to estimate EA is given by Glockler's formula[12,13]

$$EA = IP(Z_-) = 3IP(Z_0) – 3IP(Z_1) + IP(Z_2)$$

where $Z_0$, $Z_1$, $Z_2$ are the atomic numbers of the neutral atom and the singly and doubly charged positive ions of the isoelectronic sequence. Application of Glockler's formula results in the same trend in EA as the √IP plot, that is, the EA of Pt is found to be greater than those of Ni and Pd by about 1 eV. (ii) The valence orbital ionization energies (n –

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1)$d^9 ns$ → $(n - 1)d^9$ and $(n - 1)d^9 np$ → $(n - 1)d^9$ show that whereas the values for Ni and Pd are nearly equal in each valence orbital ionization energy (VOIE), the corresponding VOIE for Pt is about 1 eV larger for both the n$s$ and n$p$ ionization.[14] This again points to the greater relative stability of the n$s$ orbital in Pt compared to Pd and Ni; it is this orbital which is involved in the electron affinity values given in the Table. (iii) The relative stability of the 6$s$ valence electrons in the third transition series is not simply a feature of the nickel triad but is maintained throughout the entire transition series. Phillips and Williams[15] have plotted the ionization energies for the removal of the two $s$ electrons from the configurations $3d^{n-2} 4s^2$, $4d^{n-2} 5s^2$, and $5d^{n-2} 6s^2$ in the first, second, and third transition series, respectively. The order of stability of the $s$ electrons is third series > first series > second series. They conclude that the very marked increase in the stability of the $6s^2$ electrons is a consequence of the nuclear charge increase in the lanthanide series. (iv) Atomic Hartree–Fock calculations[16–18] consistently indicate that the effective nuclear charge ($Z_{eff}$) felt by the 6$s$ electrons of the third transition series is larger than $Z_{eff}$ for the 4$s$ and 5$s$ electrons in the first and second transition series, respectively. Jørgensen[19] has noted that the screening constant for heavy elements decreases because of a relativistic effect.

As regards the $\pi$ back bonding ability of the metal atoms throughout the transition series, Phillips and Williams have examined the $d^{n-1}$ → $d^{n-2}$ ionization energies in each transition series.[15] Unfortunately, there is a sparsity of data for the third transition series but they conclude that "... there appears to be a relative *lowering* of binding energy of the 5$d$ compared with 4$d$ as a consequence of the filling up of the lanthanide series". This lowering of binding energy will *increase* the capability for $\pi$ back bonding of the third-row transition elements compared to the second-row transition elements.

In summary, we see that the filling of the lanthanide series prior to the third transition series has two consequences. First, the 6$s$ orbital is stabilized providing for stronger $\sigma$ bonds and second the 5$d$ orbital is destabilized resulting in stronger $\pi$ back bonding relative to the second transition series. The effect of filling the lanthanide series on the ionic radii of third-row transition elements has been known for some time and we commonly use the term "lanthanide contraction". It has been the purpose of this correspondence to point out that the effect of filling the lanthanide series on covalent bond strength can be described in terms of the function (EA − IP).

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