Study of Core Electron Binding Energies in Some Group IIIa, Vb, and VIb Compounds [1]

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The photoelectron spectra of a number of Al, Ga, In, Tl, Nb, Ta, and W compounds were obtained using Al Kα and Mg Kα X-rays. The chemical shifts obtained for the spectra of the core electrons have been examined as a function of position in the periodic table. By selecting metals with nearly equal electronegativities and choosing structurally similar compounds, one may make comparisons of relative chemical shifts within analogous compounds. The underlying assumptions in these comparisons are critically evaluated in terms of the crystal potential. The relative chemical shifts were found in general to be proportional to the ratios of the average ionic radii of the metals.

I. Introduction

The ionization energies of core electrons can be determined by X-ray photoelectron spectroscopy by means of the familiar Einstein relationship

$$E_i = h\nu - E_e \tag{1}$$

where E_i is the ionization energy, $h\nu$ is the X-ray energy, and E_e is the kinetic energy of the ejected photoelectron. The actual core electron binding energy, which is closely related to the ionization energy, is influenced by the local electron density surrounding the atom and by the structural arrangement of the other atoms within the solid. One can observe that the core electron binding energies of a central atom vary as the valence electron density of that atom is changed through a series of different bonding conditions. This is usually referred to as a chemical shift.

Siegbahn, *et al.*,[3] originally handled their chemical shift data by plotting the core electron binding energy E_B vs. q, where q was Pauling's charge. A plot of this type often gives a straight line which is useful in identifying the approximate oxidation state of a compound. The treatment used by Siegbahn, *et al.*, worked surprisingly well for gaseous materials and covalent compounds of carbon and sulfur. This treatment has also been used by many authors in the analysis of data from inorganic solids but has not been as rewarding in general[4] as when applied to the analysis of data on gaseous or covalent compounds. In most cases the lack of success probably arises primarily because the crystal potentials of the inorganic solids have not been taken into consideration.

An attempt has been made in this paper to compare chemical shift data on some group IIIa, Vb, and VIb compounds. Rather than carrying out any extensive calculations to obtain crystal potentials, we have tried to take advantage of structural similarities. By comparing structurally similar compounds, it is possible to obtain some insight on the nature of chemical shifts as a function of position in the periodic table. A similar approach was carried out by Stec, *et al.*,[5] on a series of nitrogen, arsenic, and phosphorus compounds.

II. Experimental Section

The spectra were taken with an electrostatic electron spectrometer located in the Physics Division of the Oak Ridge National Laboratory. The spectrometer is a dispersion instrument containing double-focusing spherical sector plates. Details of its design and operation have been published elsewhere.[6] The spectra were taken with an energy resolution of 0.13% full-width half-maximum.

The samples were studied as a thin film of powder dusted onto a backing of tape. The samples were loaded under an argon atmosphere since many of the materials were hygroscopic. This was accomplished with a sample transfer device that permitted evacuation before the sample was introduced into the spectrometer. All the samples were purchased from either Alfa Chemical Co. or Research Inorganic Co. They all had listed purities of 98% or better.

The binding energies were derived from the ionization energies by comparing them to some standard material in contact with the sample. The carbon 1s peak was used as a primary standard whose binding energy was taken to be 285.0 eV.[7] This was a convenient reference since it was always present, presumably in intimate contact with the surface of the sample. The validity of using the C 1s peak as a standard in the present study was checked by mixing MoO_3 with selected samples.[8] The reproducibility of the binding energies is about ±0.3 eV.

III. Results and Discussion

A possible means of studying chemical shifts is by comparisons of binding energies of core electrons in analogous compounds. In order to understand the significance of these comparisons, one ought to evaluate the basic equation that expresses the factors involved in the changes in binding energies of core electrons. The equation can be written

$$\Delta E = (\Delta q e^2 / r) - \Delta V \tag{2}$$

where ΔE is the change in binding energy, Δq is the change in calculated charge, ΔV is the change in crystal potential in going from one compound to the next, and r is the ionic radius[9] of the ion common to both compounds.

The photoejected core electron is influenced by the poten-

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(2) (a) University of Tennessee. (b) Oak Ridge National Laboratory.

(3) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. Karlsson, I. Lindgren, and B. Lindberg, "ESCA: Atomic, Molecular, and Solid State Structure Studies by Means of Electron Spectroscopy," Almqvist och Wiksell, Uppsala, Sweden, 1967.

(4) This generalization, though subject to many exceptions, was arrived at by T. A. C. during a compilation of a bibliography on chemical shifts in X-ray photoelectron spectroscopy. It has also been remarked upon by other authors, *e.g.*, Hedman, *et al.*, in his discussion of phosphorus compounds: J. Hedman, M. Klasson, B. J. Lindberg, and C. Nordling, "Electron Spectroscopy: Proceedings of the International Conference on Electron Spectroscopy, Asilomar, Pacific Grove, Calif., Sept 1971," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 207.

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(6) B. P. Pullen, T. A. Carlson, W. E. Moddeman, G. K. Schweitzer, W. E. Bull, and F. A. Grimm, *J. Chem. Phys.*, 53, 768 (1970).

(7) U. Gelius, P. F. Heden, J. Hedman, B. J. Lindberg, R. Manne, R. Nordberg, C. Nordling, and K. Siegbahn, *Phys. Scr.*, 2, 70 (1970).

(8) W. E. Swartz, Jr., and D. M. Hercules, *Anal. Chem.*, 43, 1775 (1971).

(9) In the usual form for covalent compounds the atomic radius is used.[7] We have found that for ionic compounds the ionic radius is often preferable.[10]

(10) T. A. Carlson, G. E. McGuire, and G. K. Schweitzer, unpublished results.

tial of all the ions in the lattice as it is ejected. The crystal potential felt by a core electron can be described as

$$V = \sum_i (e^2 q_i / r_i) \tag{3}$$

where e is the electron charge and q_i is the charge on an ion in electron units at a distance r_i from the central ion.

If we wish to compare the binding energies for the core electrons of two different elements, x and y, that form a series of analogous compounds, 1, 2 . . ., the following ratios from eq 2 can be used

$$\frac{\Delta E_x}{\Delta E_y} = \frac{(\Delta q_x e^2 / r_x) - (V_1 - V_2)_x}{(\Delta q_y e^2 / r_y) - (V_1 - V_2)_y} \tag{4}$$

If the change in crystal potentials $(V_1 - V_2)$ is small and $\Delta q_x = \Delta q_y$, then

$$\Delta E_x / \Delta E_y \cong r_y / r_x \tag{5}$$

The electronegativities of the metals chosen for study are as follows: Al, 1.5; Ga, 1.6; In, 1.7; Nb, 1.6; Ta, 1.5; W, 1.7. Thus, the Δq's calculated from these electronegativities for similar compounds would be nearly the same, so the assumption that $\Delta q_x \cong \Delta q_y$ is valid.

In order to evaluate the importance of V, the crystal potentials were calculated for a few cases where the crystal structures are easily available from Wyckoff.[11] These calculations were based on a program written by Picken and Van Gool.[12] Bond distances and calculated charges based on Pauling's electronegativity scale[13] were used as input to the program. The results are listed in Table I. We see from the differences in V between AlF_3 and $AlCl_3$ that $V_1 - V_2$ is not negligible. However, it may also be noted that the differences in V_x vs. V_y (for example: $AlCl_3$ vs. $InCl_3$, AlF_3 vs. GaF_3, and $NbCl_5$ vs. $TaCl_5$) are not excessive. Thus, if $\Delta V_x \cong \Delta V_y$, and ΔV_x, ΔV_y are linear functions of ΔE_x, ΔE_y, a linear relationship can occur when ΔE_x is plotted against ΔE_y for an analogous series of compounds. In addition, the slope of $\Delta E_x / \Delta E_y$ will reflect the relative size of the ionic radius, although the magnitude of the slope will be altered by the crystal potentials.

From the above discussion it can be seen that a plot of the binding energies for pairs of analogous compounds will yield a simple linear plot under special conditions. The method cannot be relied upon to give a quantitative evaluation of the relative chemical shift defined as $\Delta E_x / \Delta E_y$ by way of eq 5. However, one still may be able to predict the order of the relative chemical shift.

In Tables II and III are listed the binding energies of the core electrons of the metal ions for the various compounds we studied. At the present time there is relatively little published in the literature on the binding energy shifts for the elements chosen for study here. Nefedov, et al.,[14] have reported on a number of aluminum compounds, Novakov and Geballe[15] have looked at some intermetallic niobium compounds, and Jorgensen[16] has examined a group of thallium

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(15) T. Novakov and T. H. Geballe, *Solid State Commun.*, **10**, 225 (1972).

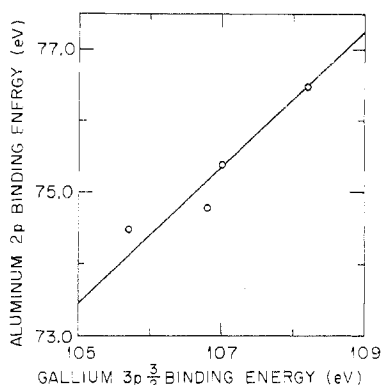(16) C. K. Jorgensen, *Theor. Chim. Acta*, **24**, 241 (1972).

Table I. Calculated Crystal Potentials

Compd	Site	Charge[a]	Crystal potential,[b] eV
$AlCl_3$	Al	1.29	−10.34
$InCl_3$	In	1.03	−7.52
AlF_3	Al	2.37	−26.08
GaF_3	Ga	2.29	−23.93
$NbCl_5$	Nb	1.94	−13.74
$TaCl_5$	Ta	2.15	−15.10

[a] The charge assigned to the ions are based on the method of Pauling.[13] [b] The crystal potential that a core electron feels at the site indicated was calculated by a program written by Picken and Van Gool.[12]

Table II. Binding Energies (eV) for Group IIIa Compounds

Compd	Al 2p	Al 2s	Compd	Ga $3p_{3/2}$	Ga $3p_{1/2}$
Al	72.4	117.2	Ga_2O_3	105.7	109.1
Al(acac)[a]	73.1		Ga_2S_2	106.2	108.6
Al_2O_3	74.5	118.9	Ga(acac)[a]	106.3	109.5
AlN	74.6	119.6	Ga_2S_3	106.8	110.4
Al_2S_3	74.8	119.8	GaI_3	106.8	110.1
AlI_3	74.8		$GaBr_3$	107.0	110.1
$AlCl_3$	74.9	119.8	GaF_3	108.2	111.9
$AlBr_3$	75.4	120.0			
$LiAlH_4$	75.8	120.1			
AlF_3	76.5	121.2			
K_3AlF_6	75.6	120.6			

Compd	In $3d_{5/2}$	In $3p_{3/2}$	Compd	Tl $4f_{7/2}$	Tl $4d_{5/2}$
In	444.8	666.0	Tl_2O_3	117.7	384.9
InCl	445.1	667.4	TlI	118.7	385.6
In_2S_3	445.1	666.6	Tl_2S_3	118.9	385.5
In_2O_3	445.2	666.6	Tl_2S	118.9	385.7
In(acac)[a]	445.6	667.0	TlCl	119.2	385.9
InI_3	446.3	667.3	TlBr	119.4	386.3
InF_3	446.7	667.5	TlF	119.4	386.3
$InBr_3$	446.8	667.8			
$InCl_3$	447.1	668.2			

[a] acac = acetylacetonate.

Table III. Binding Energies (eV) for Group Vb and VIb Compounds

Compd	Nb $3d_{5/2}$	Nb $3p_{3/2}$	Compd	Nb $3d_{5/2}$	Nb $3p_{3/2}$
Nb	202.3	360.8	$KNbO_3$	206.7	365.3
NbS_2	207.9	366.0	Nb_2O_5	207.6	365.9
NbN	207.5	365.8	K_2NbF_7	209.3	367.4
$NbBr_5$	207.3	365.4	NbF_5	209.6	367.6
$NbCl_5$	208.2	366.1			

Compd	Ta 4f	Ta $4d_{5/2}$	Compd	Ta 4f	Ta $4d_{5/2}$
Ta	21.8	226.9	$TaBr_5$	27.1	231.4
$KTaO_3$	26.1	230.0	$TaSi_2$	27.2	231.3
TaS	26.8	231.1	$TaCl_5$	27.5	231.2
Ta_2O_5	26.8	230.8	TaF_5	28.0	231.8
TaS_2	26.9	231.0	K_2TaF_7	29.6	235.1
Ta_5Si_3	26.9	231.1			

Compd	W $4f_{7/2}$	W $4d_{5/2}$	Compd	W $4f_{7/2}$	W $4d_{5/2}$
W	31.8	244.2	WBr_5	36.5	247.8
WC	32.4	244.3	WO_3	36.8	248.4
WBr_6	36.1	247.9	WCl_6	37.1	248.5
Li_2WO_4	36.2	247.8	$WOCl_4$	37.4	

compounds. Only scattered data are available for compounds of the other metals.

From the data listed in Table II, separate plots (Figures 1 and 2) were made to compare the binding energies of aluminum with those of gallium and indium. Since the energy spacings in the ordinate and abscissa are equal, the plots may also be taken as a comparison of change in binding energy and the slope is equal to $\Delta E_x / \Delta E_y$. By plotting the Al 2p binding energies of the series of aluminum compounds vs. the Ga $3p_{3/2}$ binding energies of the analogous gallium compounds, one obtains a series of points for which a line with a

Figure 1. A plot of Al 2p binding energy in aluminum compounds *vs.* the Ga $3p_{3/2}$ binding energy in analogous gallium compounds.

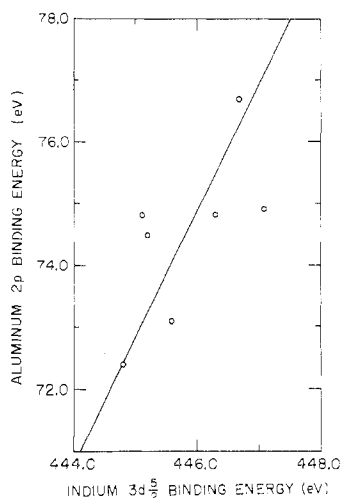**Figure 2.** A plot of Al 2p binding energy in aluminum compounds *vs.* the In $3d_{5/2}$ binding energy in analogous indium compounds.

Figure 3. A plot of Nb $3d_{5/2}$ binding energy in niobium compounds *vs.* Ta 4f binding energy in analogous tantalum compounds.

Figure 4. A plot of Nb $3d_{5/2}$ binding energy in niobium compounds *vs.* W $4f_{7/2}$ binding energy in analogous tungsten compounds.

slope of 0.94 can be drawn. This seems to indicate that the relative chemical shifts of the aluminum and gallium compounds are almost the same. In Figure 2, the slope obtained by plotting the points representing the Al 2p binding energy *vs.* the In $3d_{5/2}$ binding energy is much larger, 2.05, which might indicate that indium compounds show substantially smaller chemical shifts than aluminum compounds. However, the scatter in the data precludes any definitive statement. This may be due in part to differences in crystal structures since there are several points in Figure 2 that do not follow the general trend. For example, the apparent scatter of the oxides and sulfides reflects the fact that the structures of the oxides and sulfides of aluminum and indium exist in slightly different structural modifications.[11] Even with this scatter the results agree with Stec's conclusion that the first-row elements in group Va show the largest relative chemical shifts, while the second- and third-row elements show correspondingly smaller shifts.[5]

This same analysis applied to niobium, tantalum, and tungsten in Figures 3 and 4 gave lines with slopes of 1.05 and 1.07, respectively, which imply that each of the elements gives essentially the same relative shift. It seems unusual that the tungsten relative shifts are the same as those of niobium when tungsten has predominantly a +6 oxidation state. It is also interesting that there is less scatter in the points in the plot of the niobium binding energies *vs.* the tungsten binding energies than in the plot of the niobium binding energies *vs.* tantalum binding energies. This appears unusual since niobium and tantalum compounds have almost identical
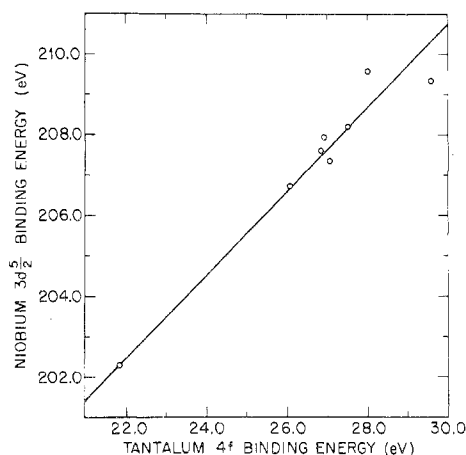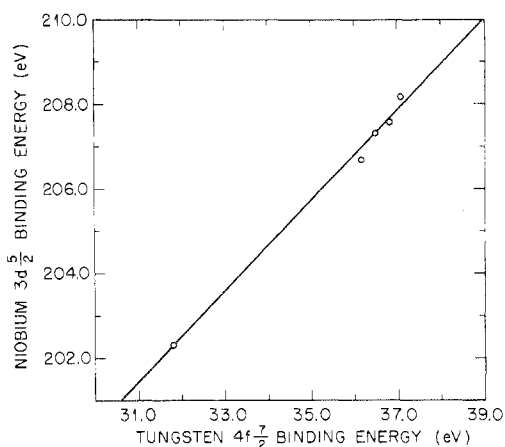
crystal structures, while the structures of tungsten compounds are not known as well but are suspected of being slightly different. The fact that tungsten is lower in the periodic chart than niobium could be offset by its higher oxidation state.

Since the bonding in these compounds has considerable ionic character, one suspects a relationship between the ionic radius and the relative chemical shifts given in eq 5. The average ionic radii for Al^{3+}, Ga^{3+}, and In^{3+} are 0.51, 0.62, and 0.81 Å, respectively.[17] From the ratios of the ionic radii one might expect Al^{3+} to be more sensitive to changes in valence electron density than Ga^{3+} and In^{3+}. This appears to agree with the plot of the Al 2p binding energies of aluminum compounds *vs.* the In $3d_{5/2}$ binding energies for analogous indium compounds. One does not anticipate a significant change in the relative shift between Al and Ga, and this is reflected in the near-unity slope of Figure 1. It is also of interest to compare the trends in the intrinsic chemical shifts of the related Nb^{5+}, Ta^{5+}, and W^{6+} compounds. The average ionic radii of Nb^{5+}, Ta^{5+}, and W^{6+} are 0.69, 0.68, and 0.62 Å, respectively. From Figures 3 and 4 it appears that Nb^{5+}, Ta^{5+}, and W^{6+} compounds tend to display similar chemical shifts in agreement with the small change in the ionic radii.

IV. Conclusion

Determinations were made of binding energy shifts of core electrons for elements that make up groups IIIa, VB, and VIb

(17) K. B. Harvey and G. B. Porter, "Introduction to Advanced Inorganic Chemistry," Addison-Wesley, Reading, Mass., 1963.

of the periodic table. Systematic correlation of the results was obtained by comparing compounds of similar structure. However, these comparisons need to be tempered by the realization of the importance that the crystal potential plays with the compounds.

# A Kinetic Study of the Permanganate–Manganous Ion Reaction to Form Manganic Ion in Sulfuric Acid Media

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The reduction of permanganate ion by manganous ion was studied in sulfuric acid media using the stopped-flow technique. All reactions were studied at two wavelengths, $\lambda = 524$ nm (loss of MnO$_4^-$) and $\lambda = 419$ nm [gain of Mn(III)]. At all experimental conditions it was observed that the rates of reactant loss and product gain agreed with each other to within ±7%. The reaction was found to obey the rate expression $-d[\text{MnO}_4^-]/dt = \frac{1}{5}(d[\text{Mn(III)}]/dt) = \{k_0 + k_1[\text{H}^+] + k_2[\text{H}^+]^2\}[\text{Mn(II)}]^2[\text{MnO}_4^-]$. The values of k_0, k_1, and k_2 were shown to be 100 M^{-2} sec^{-1}, 19 M^{-3} sec^{-1}, and 63 M^{-4} sec^{-1}, respectively.

Introduction

The reaction between manganous and permanganate ions in acid solution has been the subject of numerous investigations.[1-7] It was observed that the final product was an insoluble form of tetravalent manganese, the net reaction being

$$3\text{Mn}^{2+} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$$
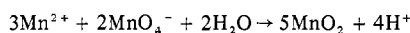
Polissar[3] noted that the reaction has an induction period, and, in addition, is autocatalyzed by the solid MnO$_2$ produced. Tompkins[7] observed that several anions, among them SO$_4^{2-}$ ion, combine with the intermediate Mn^{3+} to give an unstable complex. Adamson[5] using radioactive manganese studied the exchange rates between Mn(II) and Mn(VII), Mn(VI) and Mn(VII), and Mn(II) and Mn(III) and concluded that the rate-determining step in perchloric acid solution was the electron-exchange reaction

$$\text{MnO}^+ + \text{MnO}^{2+} \rightarrow \text{electron exchange}$$
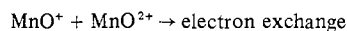
His kinetic analysis gave the expression

$$R = k[\text{H}^+]^a[\text{Mn}^{2+}]^b[\text{MnO}_4^-]^c$$

for the velocity of the rate-determining step in the exchange reaction where the approximate values of a, b, and c are $\frac{4}{3}$, $\frac{4}{3}$, and $\frac{1}{3}$, respectively. In these previous studies, the acidity and the manganous ion concentration were such as to favor the formation of solid manganese dioxide.

Kalra and Gosh[8] observed that when the acidity is high, and the Mn(II)/Mn(III) ratio is about 25 or greater in a sul-

fate medium, the reaction between permanganate ion and manganous ion occurs stoichiometrically to yield Mn(III) according to the net reaction

$$8\text{H}^+ + \text{MnO}_4^- + 4\text{Mn}^{2+} \rightarrow 5\text{Mn}^{3+} + 4\text{H}_2\text{O}$$
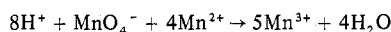
The stability of the Mn(III) produced is also dependent upon the acidity and the [Mn(II)]/[Mn(III)] ratio. When the latter ratio is at least 25 and the sulfuric acid concentration is about 4.5 M, the Mn(III) produced is stable for several months.

The procedure described by Kalra and Gosh for the preparation of Mn(III) has been used by them[8] and others[9] in kinetic studies involving Mn(III) as either a reactant or a catalyst. The present work was initiated in order to elucidate the mechanism by which Mn(III) (rather than MnO$_2$) is formed at conditions similar to those described by Kalra and Gosh.

Experimental Section

Reagents. Triply distilled water was used in the preparation of all solutions.

Baker Analyzed reagent grade potassium permanganate was used in the preparation of all permanganate in sulfuric acid solutions. These solutions were prepared just prior to use to avoid permanganate decomposition.

Manganous, Mn(II), solutions were prepared using Fisher, reagent grade MnSO$_4$·H$_2$O in sulfuric acid. In all kinetic runs the sulfuric acid concentration in the Mn(II) and the MnO$_4^-$ solutions was the same.

The total ionic strength was maintained constant at $\mu = 3.96$ M using sodium bisulfate.

Manganic ion, Mn(III), was prepared by the method of Kalra and Gosh, discussed earlier.

Spectra. All spectra were taken using a Cary 14 recording spectrophotometer.

Kinetic Measurements. Rates of reaction were followed by measuring both the decrease in absorbance of MnO$_4^-$ at 524 nm and the increase in absorbance of Mn(III) at 419 nm. The reaction was

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