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An X-Ray Photoelectron Spectroscopic Study of Volatile Vanadium Compounds

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ABSTRACT:

Vapor phase core electron binding energies were determined by X-ray photoelectron spectroscopy for nine vanadium compounds. Vanadium $2p_{3/2}$ binding energies were correlated using CHELEQ atomic charges and the "transition state" point charge potential equation. Excellent correlation was obtained for compounds which are well represented by a single valence bond structure. In the case of the other compounds, information regarding the relative contributions of various resonance structures and the importance of back-bonding was obtained by comparison of experimental and calculated binding energies.

Introduction

The CHELEQ electronegativity equalization procedure for calculating atomic charges has been successfully used, in conjunction with the point-charge potential equation, to correlate core electron binding energies for a wide range of simple organic and inorganic compounds.^{1,2} The method has been parameterized for transition metal compounds and has been used to a limited extent for such compounds,^{2,3} but no systematic study has been made of the applicability of the method outside the main-group elements. In this paper we report gas phase core electron binding energies determined by X-ray photoelectron spectroscopy for nine vanadium compounds and we discuss the nature of the bonding in these compounds as deduced from the data. This work is the first gas-phase XPS study of a series of compounds of a transition metal in which a wide range of metal oxidation states is spanned.

Experimental

Standard high-vacuum and inert-atmosphere techniques were employed. The organometallic vanadium compounds were handled under argon. All metal and glassware used in manipulation of the vanadium halides and oxyhalides was flamed under high vacuum and pretreated with the compound to be handled. Vanadium pentafluoride was prepared by the thermal disproportionation of VF_4 (Orion) in a steel bomb.⁴ The VF_5 was twice treated with activated NaF ⁵ and was stored in a bulb containing activated NaF . Vanadyl trifluoride (Alfa) was used without further purification. Vanadyl trichloride (ROC/RIC) was distilled through traps at 0, -78, and -196°. The clear liquid collected at -78° had a vapor pressure at 0° of 4.2 Torr (lit.⁶ 4.4 Torr). Vanadium tetrachloride (Orion) was distilled through traps at 0, -78, and -196°. The dark red liquid collected at -78° was stored at -78° until used. Tris(hexafluoroacetylacetonato)vanadium,^{7,8} $\text{V}(\text{hfacac})_3$, was prepared by the method of Morris *et al.*⁸ and purified by sublimation (m.p. 75.5-76.5°, lit.⁷ 76°). The $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ (Strem) (m.p. 139.5-140.5°, lit.⁹ 139°) was used without further purification. Its infrared spectrum agreed with the literature.⁹ Vanadium hexacarbonyl was prepared from $[\text{Na}(\text{diglyme})_2][\text{V}(\text{CO})_6]$ (Orion) by the method of King.¹⁰ It was stored in the dark at -78° over P_2O_5 and resublimed immediately before use. The $(\pi\text{-C}_7\text{H}_7)\text{V}(\text{CO})_3$ was prepared from $\text{V}(\text{CO})_6$ and cycloheptatriene by the method of Werner and Manastyrskyj¹¹ and was purified by sublimation. The product melted at 133-134° (lit.¹¹ 134-137°) and exhibited an infrared spectrum in agreement with the literature.¹¹ The $(\pi\text{-C}_7\text{H}_7)\text{V}(\pi\text{-C}_5\text{H}_5)$ was prepared from $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and cycloheptatriene by the method of King and Stone¹² and was purified by sublimation at 120°.

X-Ray Photoelectron Spectra. Spectra were obtained using the Berkeley iron-free, double-focusing magnetic spectrometer.¹³ The halides, oxyhalides and vanadium hexacarbonyl were irradiated in a gold plated chamber with a volume of 300 cc, a 0.5-mm exit slit and an aluminum X-ray window. Tris-(hexafluoroacetylacetonato)vanadium, $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and $(\pi\text{-C}_7\text{H}_7)\text{V}(\text{CO})_3$ were irradiated using a slit plug described by Banna.¹⁴ The sample and reference gas were handled in a system constructed of 0.5-in. stainless steel pipe. This system was assembled and secured while backflushing with argon gas as in standard Schlenk manipulation. The vapor of the compound passed to the irradiation chamber through a 15-in. length of tubing constructed of Pyrex glass and stainless steel. The samples of VCl_4 and $\text{V}(\text{CO})_6$ were held at 0° during data collection to minimize decomposition. The $(\pi\text{-C}_7\text{H}_7)\text{V}(\pi\text{-C}_5\text{H}_5)$ was held in a heated chamber¹⁴ at ca. 100° .

Magnesium K_{α} X-rays (1253.6 eV) were used for all spectra. Argon or neon at a partial pressure of 20-40 μ was introduced with the sample to the irradiation chamber, and the Ar $2p_{3/2}$ line ($E_B = 248.45$ eV) or the Ne $1s$ line ($E_B = 870.21$ eV) was used as a reference. Sample and reference data were collected alternately. In the case of $\text{V}(\text{hfacac})_3$, $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$, $(\pi\text{-C}_7\text{H}_7)\text{V}(\text{CO})_3$ and $(\pi\text{-C}_7\text{H}_7)\text{V}(\pi\text{-C}_5\text{H}_5)$, the reference was measured relative to the strongest peak in the compound and the other binding energies were determined relative to the strongest peak in a run with no reference gas present. Binding energies were determined by a least-squares fitting of the data to Lorentzian line shapes. The relative accuracy of the peak positions is about ± 0.1 eV. The reported binding energies correspond to absolute free-molecule ionization potentials.

~~Parameters for CHELCO Calculations.~~ Bond distances from electron diffraction studies were used for VF_5 ,¹⁵ VOCl_3 ,¹⁶ and VCl_4 .¹⁷ Bond distances from X-ray diffraction data were used for $(\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ ¹⁸ and $(\pi\text{-C}_7\text{H}_7)\text{V}(\pi\text{-C}_5\text{H}_5)$.¹⁹ Bond distances for $\text{V}(\text{CO})_6$, VOF_3 , and $(\pi\text{-C}_7\text{H}_7)\text{V}(\text{CO})_3$ were estimated.

Results and Discussion

Table I lists the observed binding energies. The vanadium $2p_{3/2}$ binding energies span a range of about ten electron volts. The relative ordering of the chemical shifts is that expected on the basis of the vanadium oxidation states and the electronegativities of the substituent atoms. The large difference, 5.2 eV, between the vapor phase V $2p_{3/2}$ binding energy of $C_7H_7VC_5H_5$ and that reported by Groenenboom *et al.*²⁰ is probably due to the referencing problems associated with solids.²¹

The "transition state" point charge potential method corresponds to a correlation of the binding energies with valence electron distributions halfway between those of the initial-state and core-ionized molecules, and has proved useful in correlating and calculating core binding energies.²

$$E_B = k(Q + Q_f - 1)/2 + (V + V_f)/2 + \ell \quad (1)$$

In equation 1, E_B is the binding energy for a particular core level in the ionized atom, Q is the initial charge on this atom, V is the Coulombic potential energy due to the other charged atoms in the molecule, and k and ℓ are empirical constants determined by a least-squares fit. Q_f and V_f are the values of Q and V for the core-ionized molecule; these values can be estimated using the principle of equivalent cores.²²

The vanadium $2p_{3/2}$ binding energies can be correlated with CHELEQ atomic charges using equation 1. By applying the rules which we have previously outlined² for writing valence bond structures we obtained a good correlation for all the compounds except the three carbonyl compounds. The latter compounds were ignored in the least-squares evaluation of the parameters k and ℓ .

TABLE I

Experimental Binding Energies

Compound	E _B , eV				
	V 2p _{3/2}	C 1s	O 1s	F 1s	Cl 2p _{3/2}
VF ₅	528.9 (1.22) ^a			692.6	
VOF ₃	527.1 (1.24)		539.8	692.4	
VOCl ₃	524.8 (1.10)		538.7		205.9
VCl ₄	523.7 (1.47)				205.8
V(hfacac) ₃	522.3 (2.66)	298.6 (CF ₃) 293.7 (CO) 290.9 (CH)	538.6	694.3	
(π -C ₅ H ₅)V(CO) ₄	519.6 (0.92)	292.2 (CO) 290.5 (CH)	538.7		
V(CO) ₆	518.9 (1.56)	292.0	539.7		
(π -C ₇ H ₇)V(CO) ₃	518.8 (1.41)	291.7 (CO) 290.3 (CH)	538.6		
(π -C ₇ H ₇)V(π -C ₅ H ₅)	518.5 (1.26)	289.8 ^b			

^a FWHM values in parentheses.

^b Only one C 1s line observed; FWHM = 1.02 eV.

The valence bond structures for the six compounds used in evaluating k and l for $V 2p_{3/2}$ are as follows.

Because separate electronegativity parameters for the valence d, s, and p orbitals of vanadium are not known (average parameters are used), we have not distinguished between the stereochemically different fluorine atoms in VF_5 . This procedure is reasonable in view of the facts that all five V-F distances are equal¹⁵ and that only one F 1s line is observed.

In the structures, bond orders other than unity are indicated by numbers next to the bonds. (However, in $C_5H_5VC_7H_7$, only one bond order in each set of equivalent bonds is so indicated.) The one common feature of the structures is the zero formal charge on the vanadium atom. In tris(hexafluoroacetylacetonato)vanadium, zero formal charge on the vanadium was achieved by allowing a total of only three electron pairs to be donated to the vanadium atom, corresponding to six V-O bonds of bond order 0.5. This compound could also be well fit to the binding energy data by assuming six V-O σ donor bonds of bond order unity and six V-O π back-bonds of bond order $\frac{1}{6}$. However, the latter description of the bonding is unrealistic for two reasons. First, the fact that transition metal acetylacetonates are generally high-spin complexes²³ is inconsistent with extensive back bonding in the compounds. Second, we have measured the core binding energies of several other metal hexafluoroacetylacetonates and have found that the oxygen and carbon 1s binding energies do not vary within experimental error. If back bonding were significant in these compounds, the degree of back bonding and the charge on the ligand atoms would be expected to change markedly, resulting in substantial chemical shifts.

In $(\pi C_7H_7)V(\pi-C_5H_5)$ the carbon-vanadium distances are all equal within experimental error¹⁹ and the C 1s photoelectron spectrum gave only one narrow line (FWHM = 1.02 eV). Consideration of these data led us to assume a bonding model in which each carbon-vanadium bond has the same bond order $\frac{5}{12}$, involving a σ donor bond of order $\frac{5}{24}$ and π back-bond of order $\frac{5}{24}$.

Figure 1 shows a plot of calculated versus experimental $V 2p_{3/2}$ binding energies. The calculated values were obtained from equation 1 using the least-squares evaluated parameters, $k = 22.98$ and $\ell = 514.30$. At first sight, the value of k seems rather high (compare, for example, the similarly evaluated k values of 18.24 and 15.87 for chlorine and germanium respectively).² However, it must be remembered that, according to simple theory,²⁴ k is expected to be inversely proportional to atomic radius, and, because the k value for vanadium was determined using compounds in which the vanadium atoms have high oxidation states and low effective radii, we believe the k value is reasonable.

Table II lists the calculated atomic charges and the differences between the experimental and calculated binding energies for the vanadium atoms and the ligand atoms in some of the compounds. The ligand atom binding energies were calculated using k and ℓ values which had been previously determined from data for a large number of compounds.² The fact that the binding energies calculated for the ligand atoms are in good agreement with the experimental values is strong support for the validity of the bonding assumptions and the CHELEQ charges.

The most straightforward model for the bonding in $V(CO)_6$ employs a full sigma bond and a $\frac{5}{12}$ pi back bond, the maximum possible, in each vanadium carbon bond. This model places a -3.5 formal charge on the vanadium atom and leads to a calculated vanadium binding energy much more negative than the experimental value. The calculated and experimental binding energies can be brought into exact agreement by decreasing the carbon-vanadium sigma bond order to 0.307 while maintaining the π bond order at $\frac{5}{12}$, or 0.417. The formal charges and overall bond orders in this model are:

TABLE II

Calculated Atomic Charges and Comparison of Experimental and
Calculated Binding Energies

	Q _o	E _B (expt) - E _B (calc), eV
<u>V</u> F ₅	1.122	-0.1
<u>V</u> F ₅	-0.224	0.3
<u>V</u> OF ₃	0.995	-0.3
<u>V</u> OF ₃	-0.228	0.1
<u>V</u> OF ₃	-0.310	-0.8
<u>V</u> OCl ₃	0.829	-0.1
<u>V</u> OCl ₃	-0.170	0.1
<u>V</u> OCl ₃	-0.319	-0.3
<u>V</u> Cl ₄	0.702	-0.3
<u>V</u> Cl ₄	-0.176	0.0
<u>V</u> (hfacac) ₃	0.774	0.9
(π-C ₇ H ₇) <u>V</u> (π-C ₅ H ₅)	0.464	-0.2
(π-C ₇ H ₇) <u>V</u> (π-C ₅ H ₅)	-0.054	-0.8
(π-C ₇ H ₇) <u>V</u> (π-C ₅ H ₅)	-0.054	-0.1
<u>V</u> (CO) ₆	0.347	0.0

By making similar arbitrary, but reasonable, assumptions regarding the bonding in $C_7H_7V(CO)_3$, it is possible to obtain agreement between the observed and calculated V $2p_{3/2}$ binding energies. However, in the case of $C_5H_5V(CO)_4$, such agreement can only be obtained by assuming a rather high formal charge on the vanadium atom. We have no explanation for the anomalously high V $2p_{3/2}$ binding energy in the latter compound.

The fact that in the case of $V(CO)_6$ we found it necessary to assume that the V-C sigma bond order is less than the V-C pi back-bond order, whereas in the case of $C_7H_7VC_5H_5$ we obtained a good fit assuming equal bond orders for the V-C sigma and pi bonds is consistent with modern ideas regarding the bonding in transition metal carbonyls and organometallic compounds. It is generally agreed that the CO ligand is a stronger back-acceptor than the $\pi-C_5H_5$ group.^{25,26} Indeed both theoretical²⁷ and experimental²⁸ results indicate that metal-olefin bonds are essentially nonpolar, whereas theoretical calculations²⁹ indicate that the metal atoms in metal carbonyls have quite positive charges.

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Figure Caption

Figure 1. Plot of experimental vanadium $2p_{3/2}$ binding energies versus binding energies calculated by equation 1. Standard deviation, 0.46 eV; correlation coefficient, 0.992.

Fig. 1.

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