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Preliminary communication

ELECTRON SPECTROSCOPY OF SOME CYCLOPENTADIENYLCYCLOHEPTATRIENYLMETAL COMPOUNDS

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Summary

X-ray photoelectron spectra of $(C_5H_5)M(C_7H_7)$ with M = Ti, V, Cr and some related compounds are reported. Data show that the oxidation state of the metal increases in the sequence Cr < V < Ti.

From metallation reactions on $(C_5H_5)M(C_7H_7)$ with M = Ti, V, Cr it has been concluded that the negative charge on the carbon atoms of the seven-membered ring increases in the sequence Cr < V < Ti [1]. The negative charge on the carbon atoms of the five-membered ring increases slightly in the same sequence. Consequently, an increase of the oxidation state of the metal is expected in the sequence Cr < V < Ti. Information on this oxidation state can be obtained from X-ray photoelectron spectroscopy (ESCA) [2]. A well-established relation exists between core-level binding energies (E_B) and the charge associated with the atom concerned, an increase of the positive charge on the atom resulting in an increase of the binding energies of the core-levels.

We report preliminary results of ESCA measurements on $(C_5H_5)M(C_7H_7)$ (M = Ti, V, Cr) and some related compounds. The measurements were performed with an AEI ES-200 photoelectron spectrometer, employing Mg-K_α radiation (1253.6 eV). The compounds were inserted into the vacuum chamber in a capillary and sublimed (at temperatures of 50—180° and $5 \cdot 10^{-8}$ mm Hg) onto the copper sample holder, which was cooled to —40°; the vacuum was $5 \cdot 10^{-9}$ mm Hg during the measurements.

In Table 1 the binding energies of the 2*p* and 3*s* levels of Cr in some compounds are given. Assuming oxidation states of zero and three for Cr metal and Cr_2O_3, respectively, the oxidation states of the other compounds can be estimated by linear interpolation. Although this approximation leads to somewhat overestimated charges, it has proved to be a reasonable method to show trends in oxidation states of related compounds [3]. The binding energies given in Table 1 show that the oxidation state of the metal in $(C_5H_5)_2Cr$ is considerably higher

TABLE 1

CORE-LEVEL BINDING ENERGIES OF SOME Cr COMPOUNDS (in eV)

Compound	Cr			C ^{b}	Cl	ox. state
	$2p_{1/2}$	$2p_{3/2}$	$3s$	$1s$	$2p_{1/2}2p_{3/2}$	Cr
$CpCrCl_2$ ^{a}	586.8	577.2	80.5; 76.3	285.9 (1.8)	200.3	+2.5
Cp_2Cr ^{d}	585.0	575.5	78.2; 75.6	285.5 (1.5)		+1.0
$CpCrC_7H_7$	584.0	574.8	75.5	285.0 (1.2)		+0.4
Cr_2O_3 ^{a}	587.2	577.8				+3.0 ^{c}
Cr	583.5	574.3				+0.0 ^{c}

[a] Paramagnetic; multiplet splitting is observed for 3s of the metal, while all other lines are broadened. [b] Line widths (in eV) are given in brackets. [c] Assumed values.

TABLE 2

CORE-LEVEL BINDING ENERGIES OF SOME V COMPOUNDS (in eV)

Compound	V			C ^{b}	Cl		ox. state
	$2p_{1/2}$	$2p_{3/2}$	$3s$	$1s$	$2p_{1/2}$	$2p_{3/2}$	V
Cp_2VCl ^{a}	522.2	514.2	69.6; 67.6	285.2 (1.4)	200.1	198.6	+ 1.9
Cp_2V ^{a}	521.2	513.2	69.5; 67.0	285.1 (1.5)			+ 0.7
$CpVC_7H_7$ ^{a}	521.1	513.3	68.0; 67.0	284.8 (1.3)			+ 0.8
VO_2		516.0					+ 4.0 ^{c}
V		512.6					+ 0.0 ^{c}

[a,b] and [c] see Table 1.

TABLE 3

CORE-LEVEL BINDING ENERGIES OF SOME Ti COMPOUNDS (in eV)

Compound	Ti			C ^{b}	Cl		ox. state
	$2p_{1/2}$	$2p_{3/2}$	$3s$	$1s$	$2p_{1/2}$	$2p_{3/2}$	Ti
Cp_2TiCl_2	464.5	458.4	—	286.1 (1.5)	201.0	199.6	+ 2.4 ^{d}
Cp_2TiCl ^{a}	462.8	456.6	61.5; 60.8	285.6 (1.6)	201.0	199.6	+ 1.4 ^{d}
$CpTiC_7H_7$	462.2	456.1	—	285.5 (1.8)			+ 1.1
$TiCl_3$ ^{a}	465.6	459.5	63.4		200.6		+ 3.0 ^{c}

[a, b] and [c] see Table 1. [d] It was assumed that the compounds Cp_2TiCl_2 and Cp_2TiCl differ by one unit in oxidation state.

than in $(C_5H_5)Cr(C_7H_7)$. It follows that the five-membered ring in $(C_5H_5)Cr(C_7H_7)$ is more negative than the seven-membered ring.

The binding energies of some V compounds are collected in Table 2. Oxidation states of the metal are estimated as described above. The most remarkable feature is that the compounds $(C_5H_5)_2V$ and $(C_5H_5)V(C_7H_7)$ show about equal oxidation states of V. This means that in the compound $(C_5H_5)V(C_7H_7)$ each of the rings carries a negative charge of about 0.3—0.4 electrons. These values are in a good agreement with the results of M.O. calculations on these compounds. For the compounds $(C_5H_5)_2V$ and $(C_5H_5)V(C_7H_7)$ Rettig et al. [7, 4] calculated oxidation states of the metal of + 0.609 and + 0.648, respectively. The negative charges on the five- and the seven-membered ring in the compound $(C_5H_5)V(C_7H_7)$ are — 0.335 and — 0.314, respectively [4]. In the compound $(C_5H_5)_2V$ a negative charge of — 0.304 was found for each of the rings [7].

Table 3 gives the results of the measurements on some titanium compounds. Since Ti metal with a clean surface could not be obtained, $TiCl_3$ (formal oxidation state of Ti + 3.0), was taken as a reference. It was further assumed that the difference in binding energy of the $2p_{3/2}$ levels of $(C_5H_5)_2TiCl$ and $(C_5H_5)_2TiCl_2$

corresponds with an increase of the oxidation state of the metal by one unit. The value found for ΔE_B (per electron) is 1.8 eV, which is in a good agreement with the value obtained from a comparison of TiO_2 and TiO, viz. 1.9 eV per electron [5 The estimated oxidation state of the metal in the compound $(C_5H_5)Ti(C_7H_7)$ is +1.1. Therefore, the oxidation state of the metal in the compounds $(C_5H_5)M(C_7H_7)$ increases in the sequence $M = Cr < V < Ti$. It has been concluded previously, that the negative charge on the five-membered ring in the compounds $(C_5H_5)M(C_7H_7)$ increases only slightly in the sequence given [1]. Therefore, it seems reasonably to assume that the negative charge on the five-membered ring of $(C_5H_5)Ti(C_7H_7)$ will be about 0.3—0.4 electrons. This means that the seven-membered ring carries a negative charge of about 0.7—0.8 electrons.

The charge differences between the carbon atoms of the five- and seven-membered ring should also be reflected in the binding energies of the C 1*s* levels. In all the compounds $(C_5H_5)M(C_7H_7)$, M = Ti, V, Cr, only one line for the C 1*s* level was observed, but its width at half height was 1.2 eV for the Cr compound vs. 1.8 eV for the Ti compound. This indicates that the charge difference between the carbon atoms of the five- and the seven-membered ring is larger in the Ti compound than in the Cr compound, which is in agreement with the larger dipole moment of the Ti compound [1]. The observed line broadening in the paramagnetic V compound is probably due to multiplet splitting [6], resulting from delocalization of the unpaired electron [4].

From our measurement it can be derived that the oxidation state of the metals in the compounds $(C_5H_5)M(C_7H_7)$ increases in the sequence $M = Cr < V < Ti$, resulting in an increased electron density on the ligands in the same sequence. In the Cr compound the five-membered ring is more negative than the seven-membered ring; in the V compound about equal negative charges are found for the two rings; while in the Ti compound the highest negative charge is found on the seven-membered ring. These conclusions are in a good agreement with those from metallation experiments [1] and from a ^{13}C NMR investigation on this type of compounds [8]; they support our molecular orbital considerations on $(C_5H_5)M(C_7H_7)$ compounds [1].

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References

1 C.J. Groenenboom, H.J. de Liefde Meijer and F. Jellinek, J. Organometal. Chem., 69 (1974) 235.
2 K. Siegbahn, C. Nordling et al., ESCA; Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy, Almquist and Wiksells, Uppsala, 1967.
3 C.D. Cook, K.Y. Wan et al., J. Amer. Chem. Soc., 93 (1971) 1904.
4 M.F. Rettig, C.D. Stout, A. Klug and P. Farnham, J. Amer. Chem. Soc., 92 (1970) 5100.
5 L. Ramqvist, K. Hamrin, G. Johansson, A. Fahlman and C. Nordling, J. Phys. Chem. Solids, 30 (1969) 1835.
6 C. Nordling, Angew. Chem. Intern. Ed. Engl., 11 (1972) 83.
7 M.F. Rettig and R.S. Drago, J. Amer. Chem. Soc., 91 (1969) 3432.
8 C.J. Groenenboom and F. Jellinek, J. Organometal. Chem., in press.