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UV PHOTOELECTRON SPECTRA OF (CYCLOPENTADIENYL)-(CYCLOHEPTATRIENYL)-ZIRCONIUM, -NIOBIUM AND -MOLYBDENUM

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Summary

He(I) photoelectron spectra of the compounds $(C_5H_5)M(C_7H_7)$ (M = Zr, Nb, Mo) are reported. The results are compared with those for the corresponding 3*d* transition metal compounds and discussed in terms of qualitative MO considerations.

Introduction

In a recent paper Evans et al. [1] reported UV photoelectron spectroscopy (UPS) measurements on some mixed-ring sandwich compounds of 3*d* transition metals. They showed that the contribution of the e_2 ligand orbitals to the bonding increases with increasing ring size, whereas the opposite is true for the e_1 ligand orbitals. For cyclopentadienyl ligands the main contribution to the bonding is due to the molecular orbitals of π-symmetry, but for cycloheptatrienyl or cyclooctatetraene ligands this contribution is of minor importance; in these cases, δ-bonding by interaction of the d_{xy} and $d_{x^2-y^2}$ orbitals of the metal and the e_2 ligand orbitals predominates.

Since little is known about the bonding in 4*d* transition metal sandwich compounds, we studied UPS spectra of the compounds $(C_5H_5)M(C_7H_7)$ (M = Zr, Nb, Mo). To allow a comparison with the work of Evans [1], we repeated some measurements on the 3*d* metal compounds and obtained essentially the same results.

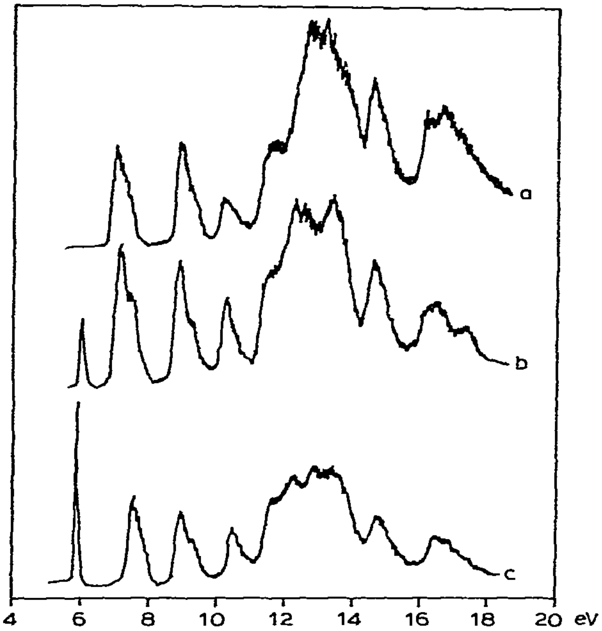

Fig. 1. He(I) photoelectron spectra of: (a) $(C_5H_5)Zr(C_7H_7)$, (b) $(C_5H_5)Nb(C_7H_7$, (c) $(C_5H_5)Mo(C_7H_7)$.

Results

The UPS spectra of the various $(C_5H_5)M(C_7H_7)$ compounds are given in Fig. 1. The higher energy regions of these spectra (i.e. the ionization range above ca. 11.0 eV) are very similar. In this range are found ionizations from orbitals corresponding to the σ-orbitals of the ligands. Considerable differences between the spectra of the various compounds are observed in the lower energy range (see Table 1) and the discussion will be limited to this region. The ionization energies in this region can be assigned as described by Evans et al. [1] for the corresponding *3d* transition metal compounds.

(i) $(C_5H_5)Mo(C_7H_7)$

Below ca. 11.0 eV the spectrum of $(C_5H_5)Mo(C_7H_7)$ shows four well separated ionization bands (Fig. 1c). The first band at 5.87 eV is sharp and is assign-

TABLE 1

IONIZATION ENERGIES OF SOME $(C_5H_5)M(C_7H_7)$ COMPOUNDS (eV)

M = Ti	Zr	Nb	Mo	Assignment
		5.98	5.87	σ
6.95	6.94	7.11	7.55	δ
		7.50		
8.78	8.89	8.78	8.93	π
9.23	9.26	9.13	9.28	
10.3	10.2	10.4	10.4	π

ed to ionization from the a_1' molecular orbital, which has mainly $4d_{z^2}$ character. The second band at 7.55 eV can be assigned to ionization from the molecular orbitals of δ-symmetry. These orbitals mainly consist of the e_2 orbitals of the C_7H_7 ring and the $4d_{x^2-y^2}$ and $4d_{xy}$ orbitals of the metal. The following two bands are due to ionization from the molecular orbitals of π-symmetry. The third band at 8.93 eV with a slight shoulder at 9.28 eV strongly resembles, in position and shape, the band assigned to the ionization from the e_1 orbitals of the metallocenes. Therefore, this band is assigned to the ionization from the molecular orbitals formed by the $4d_{xz}$ and $4d_{yz}$ orbitals of the metal and the e_1 orbitals of the C_5H_5 ring. The fourth band at about 10.4 eV is probably due to the e_1 orbitals of the C_7H_7 ring which are slightly stabilized by interaction with the $4d_{xz}$ and $4d_{yz}$ metal orbitals.

(ii) $(C_5H_5)Nb(C_7H_7)$

$(C_5H_5)Nb(C_7H_7)$ is a 17-electron compound with one unpaired electron [2]. The UPS spectrum (Fig. 1b) shows a sharp band at 5.98 eV. This band is again assigned to ionization from the a_1' molecular orbital, which is now occupied by one electron. The next two ionization bands at 7.11 and 7.50 eV overlap, but can be clearly distinguished. They are assigned to ionization from the molecular orbitals of δ-symmetry; in this paramagnetic compound ionization of an electron from a fully occupied orbital gives rise to triplet and singlet ion states in ratio 3/1 [3]. The two bands at 8.78 (shoulder at 9.13 eV) and 10.4 eV strongly resemble those of the Mo compound and are assigned in the same way.

(iii) $(C_5H_5)Zr(C_7H_7)$

$(C_5H_5)Zr(C_7H_7)$ is a diamagnetic 16-electron compound [2] which implies that the highest occupied molecular orbitals in the ground state are the bonding orbitals of δ-symmetry. Therefore, the first band of the spectrum (Fig. 1a) at 6.94 eV is assigned to ionization from these orbitals. The two other bands at 8.89 (with a shoulder at 9.26 eV) and 10.2 eV are characteristic for ionization from the molecular orbitals of π-symmetry, formed by the appropriate metal orbitals and the e_1 ligand orbitals of the C_5H_5 and C_7H_7 ring, respectively, as is the case of the Mo compound.

Discussion

The data in Table 1 show that the ionization energy of an electron from the molecular orbitals of π-symmetry is rather insensitive to change of metal, which indicates that these orbitals are mainly ligand orbitals. Indeed, no multiplet splitting is observed for the paramagnetic Nb compound. Similar results have been found for the corresponding 3*d* transition complexes [1]. The ionization energy of the electrons in the molecular orbitals consisting of metal orbitals and the e_1 orbitals of the C_5H_5 ring is ca. 0.1 eV higher for the 4*d* than for the 3*d* metal complexes. This suggests a somewhat stronger interaction between the metal orbitals and the e_1 orbitals of the C_5H_5 ring in the 4*d* than in the 3*d* compounds.

In Fig. 2 the variation in ionization energy of the molecular orbitals of π-

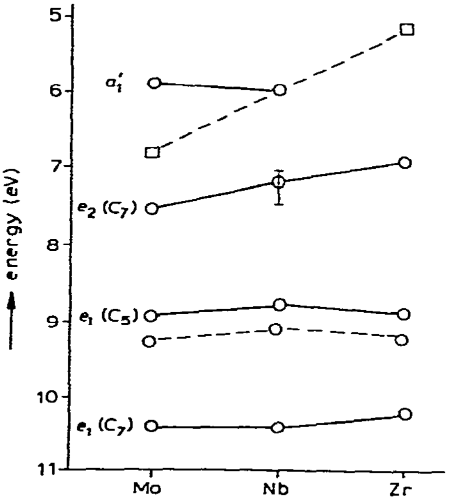

Fig. 2. Ionization energies of the a'_1 e_2 and e_1 molecular orbitals (○) and estimated energies of singly occupied a_1 molecular orbitals ( ) of the isotypic compounds $(C_5H_5)M(C_7H_7)$ (M = Zr, Nb, Mo).

and δ-symmetry and the a_1' molecular orbital is illustrated. For the paramagnetic Nb compound, ionization from the molecular orbitals of δ-symmetry gives rise to two ion states. The ionization energies are weighted according to the degeneracies of the ion states and the average is plotted, while the separation of the two states is indicated by a bar terminating in the two observed ionization energies. It is seen that the ionization energy of the molecular orbitals of δ-symmetry increases slightly with increasing group number of the metal. Similar effects were found for the corresponding *3d* transition metal compounds [1]. Since the ionization energy of the *3d* orbitals of the metal increases much more pronouncedly with increasing group number, Evans et al. [1] concluded that in the compounds $(C_5H_5)M(C_7H_7)$ (M = Ti, V, Cr) both metal and ligand contribute substantially to the molecular orbitals of δ-symmetry.

The energies of the *d* orbitals in the *4d* transition metal series show the same trend, as is seen by comparing the ionization energies of an electron from the nearly non-bonding a'_{1g} orbitals in $(C_6H_6)_2Mo$ [1] and $(C_5H_5)_2Ru$ [4], viz. 5.52 and 7.63 eV, respectively. We conclude that in the compounds $(C_5H_5)M(C_7H_7)$ (M = Zr, Nb, Mo) also, both metal and ligand contribute substantially to the molecular orbitals of δ-symmetry; this agrees with the observation of multiplet splitting for the ionization from these orbitals in the paramagnetic Nb complex.

A remarkable difference between the *3d* and *4d* transition metal series is found for the a_1' orbital. For the *3d* metal compounds $(C_5H_5)M(C_7H_7)$ the ionization energy of this orbital decreases markedly when going from M = V to M = Cr [1], whereas only a slight decrease is observed for the corresponding *4d* metal (M = Nb, Mo) complexes, viz. 0.83 vs. 0.12 eV. This difference probably arises from the smaller pairing energy of the electrons in *4d* transition metals than in the *3d* series. Due to the increase of the electron—electron repulsion upon the change from a 17-electron compound with an $(a'_1)^1$ configuration to an 18-electron compound with an $(a'_1)^2$ configuration, the ionization energy of the a_1' orbital will decrease. This decrease can be estimated for the chromium compounds: for the 17-electron compound $(C_5H_5)Cr(C_6H_6)$ an ionization energy of 7.15 eV was found for the a_1' orbital, whereas for the 18-electron compound $(C_5H_5)Cr(C_7H_7)$ a value of 5.59 eV was measured [1]. This means that the pairing energy is about 1.6 eV, which indicates that the a_1 orbital is essentially localized on the *3d* transition metal [5]. For the *4d* transition metal compounds smaller values are expected, because of the smaller electron—electron repulsion in the more diffuse *4d* metal orbitals. Comparison of our Mo and Nb compounds with the Cr and V compounds suggests that the pairing energy for Mo is 0.7 eV less than for Cr. Ionization from a singly occupied a_1' orbital of a Mo compound would occur at ca. $5.9 + 0.9 = 6.8$ eV. If the energy of the a_1' orbital is extrapolated linearly in the series $(C_5H_5)M(C_7H_7)$ (M = Mo, Nb, Zr), ionization from a singly occupied a_1' orbital of a Zr complex would be expected at ca. 5.1-5.2 eV. (A similar extrapolation for the series $(C_5H_5)M(C_7H_7)$ with M = Cr, V, Ti leads to an expected ionization energy of 5.6-5.7 eV for a singly occupied a_1' orbital in a Ti complex, which compares well with the value of 5.67 eV observed for $(C_5H_5)Ti(C_8H_8)$ [1].) This extrapolation is indicated in Fig. 2 by a dotted line. The slope of the line connecting the ionization energies of the δ orbitals of $(C_5H_5)M(C_7H_7)$ with M = Mo, Nb, Zr is intermediate between that of the dotted line and that of ionization from the π orbitals, which are essentially ligand orbitals, again confirming the composite nature of the δ molecular orbitals.

Experimental

The compounds $(C_5H_5)M(C_7H_7)$ (M = Zr, Nb, Mo) [2] and $(C_5H_5)Ti(C_7H_7)$ [6] were prepared by published procedures. The UPS spectra were recorded on a Perkin—Elmer PS-18 instrument with a heated insert probe. The compounds $(C_5H_5)M(C_7H_7)$ with M = Ti, Nb, Mo were heated at ca. 90°C and the Zr compound at ca. 130°C during the measurements. The spectra were calibrated by admixture of Ar and Xe. The errors in ionization energies are about 0.05 eV for the sharp and about 0.1 eV for the broad bands.

Acknowledgements

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