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X-RAY PHOTOELECTRON SPECTRA OF POLYHYDRIDO COMPLEXES OF TUNGSTEN AND MOLYBDENUM

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Summary

X-Ray photoelectron spectroscopy has been applied to study MH_4L_4 (M = W or Mo, L = $PHPh_2$, $PMePh_2$, $PEtPh_2$, $PBuPh_2$, PEt_2Ph, $P(OPr\text{-}i)_3$ or 1/2 dppe). It has been shown that tungsten in these compounds has a negative charge whereas the charge of molybdenum is almost zero.

Introduction

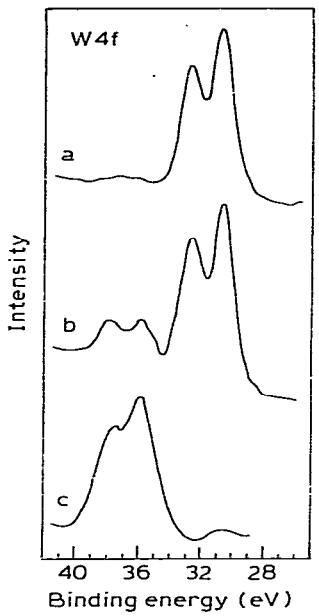
The preparation methods of the compounds with general formula MH_4L_4 (M = W or Mo, L = $PHPh_2$, $PMePh_2$, $PEtPh_2$, $PBuPh_2$ or PEt_2Ph) are known [1—3]. Such complexes are interesting in view of coordinated hydrogen atom activity in various reactions. The strength of M—H coupling and, therefore, hydrogen activity depends on the charge value of the metal atom.

X-Ray photoelectron spectroscopy (XPS) reveals such an ion property as effective charge because of the correlation between the binding energy of the core level and the calculated charge of the element in different compounds found [4].

In this paper we present results of XPS measurements of core level energies of tungsten and molybdenum hydrido complexes.

Results and discussion

The situation for the W(4*f*) line of the compounds under study is illustrated in Fig. 1. Curve a shows the W(4*f*) line for $WH_4(PEtPh_2)_4$. The interaction of



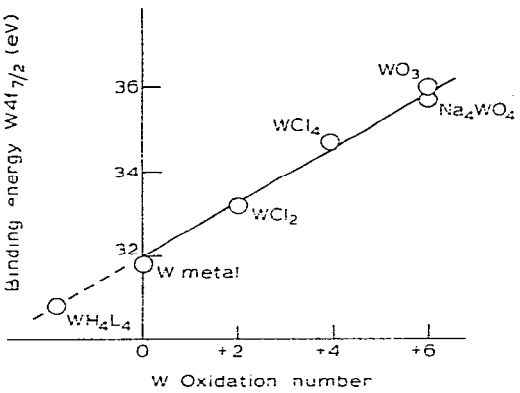


Fig. 1. X-Ray photoelectron spectra of W(4*f*) level for (a) $WH_4(PMePh_2)_4$, (b) $WH_4(PMePh_2)_4$ after air exposition, (c) WO_3.

Fig. 2. Binding energy of W($4f_{7/2}$) level as a function of tungsten oxidation number.

the sample with air gives rise to the additional high binding energy line (curve b). However it was found that the exposure to air for 20 min did not result in a marked change of the initial line position. The initial W(4*f*) line disappears completely after 5 h for some complexes. At the time when the new line intensity is still small, the complex decomposition is related, amongst other reasons, with the decrease of the P/M ratio. This may be calculated from XPS. It should be noted that the spectrum of WH_4L_4 is sharper than that of WO_3 (curve c). This fact is probably due to the purity of the compounds.

The binding energy W($4f_{7/2}$) for the product of tetrahydridotetrakis(phosphine)—tungsten(IV) decomposition is 5 eV higher than that for the complex itself. It is contradictory to the fact that the chemical shift between WO_3 and W metal was found to be equal to 4.2 eV [5—8]. The dependence of W($4f_{7/2}$) binding energy on tungsten oxidation number is linear [7]. According to this dependence (Fig. 2), the lines W($4f_{7/2}$) (36.1 eV) observed for completely oxidized complexes are due to W^{6+} ions, and the lines with the W($4f_{7/2}$) binding energy less than 30.6 eV may be assigned to the negatively charged ions.

The conclusion about the negative charge on tungsten in hydrido complexes is unaltered if the P(2*p*) line (in ligands which have been established to be a good internal standard) [9,10] is used as reference line.

The charge of the central ion for molybdenum tetrahydrides has been found to be about zero as the binding energies of Mo($3d_{5/2}$) level in the complexes are equal to that in Mo metal (Table 1).

More evidence for a negative charge on tungsten is the chemical behaviour of

TABLE 1

ELECTRON BINDING ENERGIES (eV) FOR POLYHYDRIDO COMPLEXES OF TUNGSTEN AND MOLYBDENUM

Abbreviations: dppe, $(C_6H_5)_2PCH_2CH_2P(C_6H_6)_2$; Me, CH_3; Et, C_2H_5; Pr-i, i-C_3H_7; Bu, n-C_4H_9; Ph, C_6H_5

	W ($4f_{7/2}$)	P ($2p$)
$WH_4(PHPh_2)_4$	30.9	131.4
$WH_4(PMePh_2)_4$	30.8	131.1
$WH_4(PEtPh_2)_4$	30.6	130.9
$WH_4(PBuPh_2)_4$	30.8	131.2
$WH_4(PEt_2Ph)_4$	30.7	130.9
$WH_4[P(OPr\text{-}i)_3]_4$	30.8	132.7
$[WH_5(PMePh_2)_4]^+Cl^-$	31.3	131.5
$[WH_5(PEt_2Ph)_4]^+Cl^-$	31.1	131.3
W metal	31.8	
	Mo ($3d_{5/2}$)	P ($2p$)
$MoH_4(PMePh_2)_4$	227.6	131.1
$MoH_4(PEtPh_2)_4$	227.6	130.9
$MoH_4(dppe)_2$	227.5	130.9
Mo metal	227.6	
dppe		130.9
PPh_3		131.9
$OPPh_3$		132.7

tetrahydrides. The negative charge may promote the donor character of the orbital filled by two tungsten(IV) electrons. With this condition, WH_4L_4 may react with L′ to give WH_4L_4L' provided L′ has a proper acceptor orbital and steric difficulties are absent. Actualy WH_4L_4 may be readily protonated to give the pentahydrido species $[WH_5L_4]^+$, which has been found recently [11,12].

In contrast to WH_4L_4 a similar reaction was not found for MoH_4L_4, which agrees with absence of the negative charge on molybdenum in the compounds under study.

We have also found that protonation of WH_4L_4 resulted in the increase of W($4f_{7/2}$) binding energy (Table 1).

In conclusion it is worth noting that binding energies of Mo($3d_{5/2}$) and W($4f_{7/2}$) in tetrahydrides are unusually small for molybdenum(IV) and tungsten-(IV).

Physical measurements

Photoelectron spectra, induced by MgK_α radiation (1253.6 eV), were measured with the Varian IEE-15 instrument. The C(1s) line was used as a reference line and the binding energy was taken to be 285.0 eV.

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