Determination of charge-transfer electron transitions in tungsten tetrahydride complexes stabilized by organophosphorus ligands by X-ray photoelectron and UV absorption spectra

A. P. Pivovarov

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: 007 (096) 515 3588

A change in the energy of the long-wave transition in the UV absorption spectra of tetrahydride complexes WH_4L_4 is equal to the change in the energy of the internal 2p-level of phosphorus. Based on the correlation determined, the electron transitions related to the long-wave absorption bands in the UV spectra were assigned to the charge-transfer transitions from the organophosphorus ligand to tungsten.

Key words: photochemistry, X-ray photoelectron spectra, UV absorption spectra, coordination compounds.

It has been shown previously that irradiation of molybdenum and tungsten phosphinehydride complexes results in their photoreductive dehydrogenation and formation of coordinationally unsaturated species that are capable of reacting efficiently with different molecules, including sufficiently inert ones.[1–7] For example, coordinationally unsaturated species form complexes with N_2 that can efficiently reduce coordinated nitrogen to hydrazine under the action of HCl.[1–3] Different phosphinecarbonyl complexes are obtained in an atmosphere of CO.[4] In benzene and cyclohexane, the solvent molecules are inserted into the metal—carbon bond, resulting in the oxidative addition products.[5]

Coordinationally unsaturated species formed during photolysis can also enter intramolecular reactions of oxidative addition of aryl or alkyl substituents of phosphine ligands.[6]

Under irradiation, CO_2 in the coordination sphere of the metal is reduced to formate, which gives formaldehyde or formic acid under the action of an acid (HCl, H_2SO_4).[7]

In this connection, it is of interest to study the mechanism of photoreductive dehydrogenatation of phosphinehydride complexes. For this purpose, the nature of the levels related to long-wave absorption bands for several tungsten complexes WH_4L_4, where L = PEt_2Ph, $PEtPh_2$, $PMePh_2$, $PHPh_2$, $P(OPr^i)_2Ph$, $P(OPr^i)_3$, was studied in this work by X-ray photoelectron (XP) and UV absorption spectroscopy.

Experimental

Phosphinehydride complexes WH_4L_4 were obtained by a known procedure[8] and purified by recrystallization from a benzene—methanol mixture. Cyclohexane was purified by treatment with oleum followed by rectification and dried by distillation over metallic sodium. All operations in preparation of samples for recording XP and UV spectra were carried out in a metallic box filled with argon from which oxygen and moisture had been removed. UV spectra were recorded on a Specord M-40 spectrophotometer. XP spectra were recorded on IEE 15 and PHI 555 spectrometers.

Results and Discussion

The results of studying the XP and UV absorption spectra of complexes **1—6** are presented in Table 1.

The high values of the extinction coefficients ε_{max} = 8000 ± 2000 L mol^{-1} cm^{-1} and half-widths of the absorption bands $\Delta\nu_{1/2}$ = 5400 ± 900 cm^{-1} can be evidence that the electron transitions related to these absorption bands in the UV region presumably belong to charge-transfer transitions (CT).

A substantial increase in the energy of the 2p-level of phosphorus is observed in the XP spectra in a series of complexes **1—6**. At the same time, the energy of the internal levels of $W_{4f7/2}$ changes insignificantly. This is due to the fact that the electron density decreases and, hence, the positive charge on the phosphorus atom increases as the electron-withdrawing ability of the substituents increases. According to the theory of XP spectroscopy,[9] this results in an increase in the energy of all intraatomic levels of phosphorus. As can be seen from the data in Table 1, there is a correlation between the energy of the 2p-level of phosphorus (E_{P2p}) and energy of the 0—0-transition in the UV region (ΔE_0^{UV}). The latter was determined from the intersection point of the tangent in the region of the maximum slope of the long-wave edge of the absorption bands with the abscissa axis.

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Table 1. XP and UV absorption spectra of complexes WH_4L_4

Compound		$E_{W4f7/2}$ /eV	E_{P2p} /eV	$\Delta E_0{}^{UV}$ /eV	ν_{max} /cm^{-1}	ε_{max} /L mol^{-1} cm^{-1}	$\Delta\nu_{1/2}$ /cm^{-1}
$WH_4(PEt_2Ph)_4$	(**1**)	30.7	130.9	2.50	23500	5900	4500
$WH_4(PEtPh_2)_4$	(**2**)	30.6	130.9	2.45	23800	7400	6000
$WH_4(PMePh_2)_4$	(**3**)	30.8	131.1	2.61	25300	8300	6300
$WH_4(PHPh_2)_4$	(**4**)	30.9	131.4	2.80	27000	7000	4700
$WH_4\{P(OPr^i)_2Ph\}_4$	(**5**)	31.0	131.8	3.04	28400	9400	5100
$WH_4\{P(OPr^i)_3\}_4$	(**6**)	30.8	132.7	4.46	41000	10300	6000

This correlation allows the charge-transfer electron transitions to be directly determined from experiment. Let us consider the scheme of the internal levels of the metal and ligand that form the coordination compound (Fig. 1).

The interaction between the valent levels of the metal M_v and ligand L_v, which are different in energy, results in the appearance of the electron CT transition $\Delta E_0{}^{UV}$ in the UV spectrum. In addition, d—d- (LF) and intraligand (IL) transitions, which for the sake of simplicity are not shown in Fig. 1, can appear.

An increase in the positive charge on the ligand atom results in an increase in the energy of its levels. In the first approximation, both intraatomic and valent (involved in the formation of the CT transitions) levels of the ligand will be shifted by the same value upon small changes in charge.[9] This is shown in Fig. 1 for the ML and M′L′ complexes.

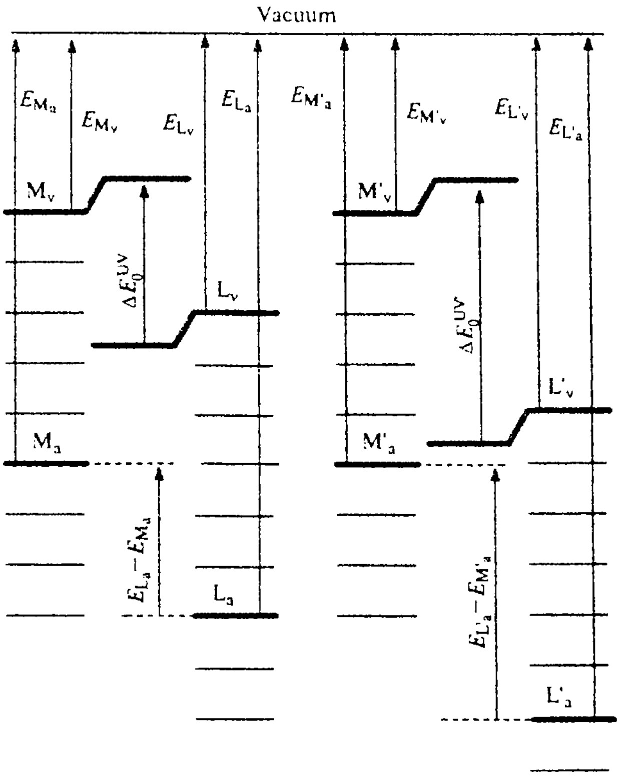

Fig. 1. Scheme of valent and intraatomic levels of metal atoms and ligands forming coordination compounds ML and M′L′.

An increase in the energy of the internal levels of the ligand results in a proportional increase in the energy of the CT 0—0-transition. It is noteworthy that the change in the energy of the ligand levels should (although to a considerably smaller extent) affect the position of the metal levels, since the valent orbitals of the metal and ligand participate in the formation of the molecular orbital in the coordination compound. This can be seen for the tungsten $W_{4f7/2}$ levels presented in Table 1. In addition, since the energy of the CT 0—0-transition in the UV absorption spectrum is the difference between the energies of the corresponding valent levels $\Delta E_0{}^{UV} = E_{L_v} - E_{M_v}$, it is more correct to consider a correlation of $\Delta E_0{}^{UV}$ with the difference in energies of the intraatomic levels of the ligand and metal in the XP spectra: $\Delta E_0{}^{XP} = E_{L_a} - E_{M_a}$.

Thus, the change in the difference in the energies of the intraatomic levels of the ligand and metal from the value $\Delta E^{XP} = E_{L_a} - E_{M_a}$ to $\Delta E^{XP\,\prime} = E_{L'_a} - E_{M'_a}$ in the XP spectra is equal to the change in the energy of the CT 0—0-transition from the value $\Delta E_0{}^{UV} = E_{L_v} - E_{M_v}$ to $E_0{}^{UV\,\prime} = E_{L'_v} - E_{M'_v}$ in the UV spectra. Therefore, this correlation can be used for identification of CT transitions in coordination compounds.

In fact, for complexes **1**—**6**, the energy of the 0—0-transition E_0 and the difference of the energies of the intraatomic levels of phosphorus and tungsten $\Delta E^{XP} = E_{P2p} - E_{W4f7/2}$ are related by a linear dependence according to the equation

$$\Delta E_0{}^{UV} = 1.17(E_{P2p} - E_{W4f7/2}) - 115$$

$$(R = 0.99465,\ SD = 0.08744,\ N = 6,\ P = 0.00004).$$

It is noteworthy that a necessary condition for the existence of this linear dependence (Fig. 2) is conservation of the same structure for all studied complexes **1**—**6**.

At present time, the structures of three octacoordinated complexes MH_4L_4 are known. Some structural data for these complexes are presented in Table 2.

Despite some difference in angles and distances, these complexes have the same structure. In these com-

Table 2. Angles (φ) and interatomic distances (*d*) in octacoordinated complexes MH_4L_4[10—12]

Compound	φ/deg,	*d*/Å	
	P—M—P	M—P	M—H
$MoH_4(PMePh_2)_4$	142.8(1)	2.433(2), 2.503(2)	1.70
$WH_4(PEtPh_2)_4$	140.0(1)	2.450(2), 2.491(2)	
$WH_4(P(OPr^i)_3)_4$	150.6(1)	2.438(3)	1.68

pounds, regardless the nature of the metal atom or ligand, the coordination polyhedron of the metal is a distorted dodecahedron with D_{2d} symmetry consisting of an embedded stretched tetrahedron formed by hydrogen atoms and a flattened tetrahedron of phosphorus atoms. Since complexes **2** and **6** are the most strongly different members of the **1**—**6** series, it can be supposed that the other compounds (**1**, **3**, **4**, and **5**) have similar structures as well.

Thus, taking into account the assumptions made, the following conclusions can be drawn. For the series of complexes **1**—**6** studied, a linear dependence between the difference of the intraatomic levels of phosphorus and tungsten $E_{P2p} - E_{W4f7/2}$ in the XP spectra and the value of the 0—0-transition ΔE_0^{UV} is observed, which was expected from the theoretical analysis (see Fig. 1). In this dependence, the value of coefficient *b* close to unity testifies that the absorption bands in the UV spectra of the complexes presented in Table 1 are related to the typical CT transitions.

The positive value of coefficient *b* indicates the following direction of the CT transition: excitation results in shifting of the electron density from the organophosphorus ligands to the tungsten atom.

It can be supposed that the experimental method described in this work can be used for determination of the nature and direction of CT transitions in other coordination compounds.

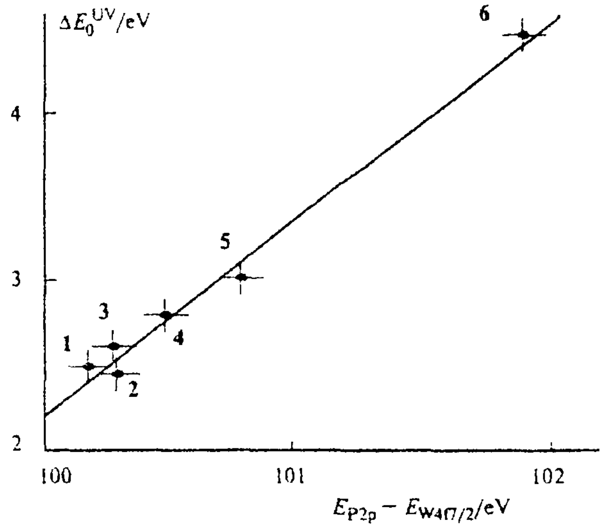

Fig. 2. Dependence of the energy of the long-wave transition ΔE_0^{UV} on the difference of energies of intraatomic levels of phosphorus and tungsten $E_{P2p} - E_{W4f7/2}$ for the series of complexes **1**—**6**.

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