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Ultraviolet Photoelectron Spectra of Some $Cr(CO)_5L$ Complexes Containing Organosulfide and Organophosphine Ligands

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Received June 16, 1977

Ultraviolet photoelectron spectroscopy (UV PES) has become an important tool for studying those transition-metal carbonyl complexes which are sufficiently volatile.[1] In this report we present the results obtained from UV PES measurements on some R_2S and R_3P complexes of $Cr(CO)_5$, providing a comparison between the electronic behavior of the R_2S and R_3P ligands, as well as the various substituents R. Although the range of complexes of this type which can be successfully used for UV PES measurements is limited by involatility on one hand and insufficient vapor-phase stability on the other hand, most of the complexes described below could be obtained in a sufficiently pure state to give good-quality spectra. While small amounts of impurity appeared in the spectra of some of the complexes (see Experimental Section), only the divinyl sulfide complex was unstable enough to prevent its handling and analysis as a pure material. Although its UV PES data showed the evidence of decomposition, useful information could still be obtained.

No UV PES study on R_2S complexes appears to have been previously reported. The spectra of $Cr(CO)_5L$ complexes (where L = NH_3, PH_3, NMe_3, PMe_3) have been measured by Lloyd.[2]

Results and Discussion

The IP values below 12 eV are listed in Table I. The observed bands are due to ionization from orbitals predominantly on the chromium and the R_2S (or R_3P) ligands, while orbitals largely CO in character give rise to peaks above 12 eV.[2,3] The splitting of the ionization from the chromium d orbitals (IP_1, IP_2) results from a breakdown of the degeneracy of the filled t_{2g} orbitals into e and b_2 components. Lloyd has assigned the first peak to the e orbital on the basis of intensity considerations,[2] but it is not clear that this is so in the present study.

The IP values obtained here may be compared with the value of 8.4 eV found for $Cr(CO)_6$.[3] Thus the R_2S and R_3P ligands appear to place a significantly greater electronic charge at the chromium site than the CO. There is no material difference between the effect of the R_2S and R_3P ligands in this respect. Results obtained from C–O stretching frequency measurements appear to present clear evidence that R_2S is a poorer π acceptor than corresponding R_3P,[4] but this difference may be compensated by a weaker σ-donor ability on the part of the R_2S ligand.[5] Graham has discussed the interrelationship between the two properties.[4]

Table I. Vertical Ionization Potentials[a] of $Cr(CO)_5L$

L	IP_1[b]	IP_2[b]	IP_3[c]	IP_4[c]
$(C_2H_5)_3P$	7.44[d]	7.58	9.67	11.1[e]
$(CH_3)_3P$[f]	7.58[d]	7.72	10.00	
$(C_2H_3)_3P$	7.52[d]	7.66	9.60	10.33[g]
$(C_2H_5)_2S$	7.45	7.67	9.71	11.48
$(CH_3)_2S$	7.59	7.79	10.00	12.10
$(C_2H_3)_2S$	7.6_1	7.8_0	9.48	
$(CH_3)(CH_2Cl)S$	7.74	7.90	10.27	

[a] In eV. [b] Assigned to the chromium d orbitals–see text. [c] Assigned to the ligand orbitals with some admixture of metal character–see text. [d] Shoulder. [e] Additional band at 11.3 eV. [f] Data taken from ref 2. [g] Assigned to the vinyl groups. Additional ligand bands at 10.76 eV and 12.0 eV.

Table II. Appropriate Ionization Potential[a] Data for R_3P and R_2S[b]

Compd	IP_1	IP_2
$(CH_3)_3P$	8.60[c]	11.3
$(C_2H_5)_3P$	8.31[c]	10.4
$(C_2H_3)_3P$	8.51[c]	9.89
$(CH_3)_2S$[d]	8.69[e]	11.20[f]
$(C_2H_5)_2S$[d]	8.46[e]	10.70[f]
$(C_2H_3)_2S$	8.42[e]	
$(CH_3)(CH_2Cl)S$	9.17[e]	

[a] In eV. [b] Data for $(CH_3)_3P$ taken from ref 9. All other values obtained in this laboratory. [c] Assigned to the lone-pair (a_1) orbital. [d] Reference 8 gives: for $(CH_3)_2S$, IP_1 = 8.67 eV, IP_2 = 11.2 eV; for $(C_2H_5)_2S$, IP_1 = 8.44 eV, IP_2 = 10.7 eV. [e] Assigned to the b_1 orbital–see text. [f] Assigned to the a_1 orbital–see text.

Table III. Increase in Ligand Orbital Ionization Energies[a] upon Complexation with the $Cr(CO)_5$ Group

Ligand	b_1	a_1
$(CH_3)_3P$		1.40
$(C_2H_5)_3P$		1.36
$(C_2H_3)_3P$		1.09
$(CH_3)_2S$	1.31	0.90
$(C_2H_5)_2S$	1.25	0.78
$(C_2H_3)_2S$	1.06	
$(CH_3)(CH_2Cl)S$	1.10	

[a] In eV.

The variation of d orbital IP values with the substituent R reflects qualitatively the ability of R to increase the electron density at sulfur or phosphorus[6] (which in turn may be passed on to chromium). Discussions of the effect of substituents directly on the donor atom are frustrated, however, by the unknown differences in the bond angle about the donor atom, with the resulting change in hybridization affecting the nature of the donor orbitals.

The remaining IP's below 12 eV are derived from ligand orbitals, with some chromium orbital character introduced as a result of complexation. Most interesting from the standpoint of the bonding between R_2S ligands and electron acceptors is the fate of the highest occupied R_2S molecular orbitals upon complexation. A sample calculation was performed on dimethyl sulfide complexed to a reference acid (in this case BH_3), using the CNDO/2 technique.[7] The B–S distance was varied in steps from 2.0 to 3.0 Å. In the uncomplexed R_2S the two highest occupied molecular orbitals are of the type[8]

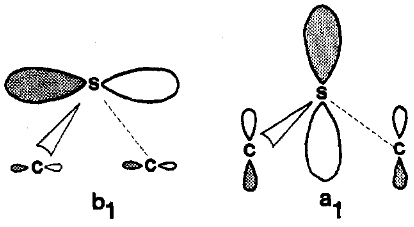

Table IV. Analytical and Infrared Spectral Data for $Cr(CO)_5L$

L	% C		% H		ν_{CO}, cm^{-1}
	Calcd	Found	Calcd	Found	
$(C_2H_5)_3P^a$	42.58	42.77	4.88	5.15	1935 s, 1945 m, 2055 w
$(C_2H_3)_3P$	43.43	43.40	2.99	2.78	1930 m, 1950 s, 2070 m
$(C_2H_5)_2S^b$					1935 m, 1945 s, 1985 w, 2060 w
$(CH_3)_2S^c$					1935 m, 1945 s, 1990 w, 2065 w
$(CH_3)(CH_2Cl)S$	29.13	29.43	1.75	1.80	1945 s,^{d} 2065 w
$(C_2H_3)_2S$					1935 m, 1945 s, 2065 w

[a] See ref 14 for reported ν_{CO} values. [b] See ref 15 for characterization of this complex. [c] See ref 16 for characterization of this complex. [d] Second peak in this region not resolved.

The b_1 orbital, essentially nonbonding, has a measured IP of 8.69 eV (Table II), while the a_1 orbital, with more bonding character than the b_1 but still highly localized on sulfur, has a measured IP of 11.20 eV. As the acid is moved closer to the ligand, the two highest occupied molecular orbitals retain essentially the configuration found for the free base, taking on acid character as the acid–base distance is lowered and tilting slightly as the distance approaches 2.0 Å. Thus it may be assumed that IP_3 and IP_4 (if measurable) in the sulfide complexes can be correlated in order with the two highest occupied molecular orbitals of the free sulfide bases, with the addition of some Cr bonding character. In the phosphine complexes, IP_3 is correlated with the lone-pair orbital (a_1) of the uncomplexed R_3P and is considered to involve Cr σ bonding.[2] On the basis of these assignments, stabilization energies are obtained for the appropriate ligand orbitals upon complexation. They are given in Table III, using the orbital designation for the uncomplexed species. The b_1 orbital is stablized by ca. 50% more than the a_1 orbital in those sulfide complexes where both IP's are measured. This is qualitatively consistent with the sample calculation, which showed the b_1 orbital stabilized by ca. twice as much as the a_1 orbital with the approach of the Lewis acid. Since the stabilization energies reflect the degree to which complexation perturbs the highest occupied ligand orbitals, the variation in stabilization energies with the changing substituent R reflects the influence of R on the ligating properties of the donor. Thus the presence of electron-donating alkyl groups results in a greater perturbation of the ligand orbitals upon complexation than with the more electron-withdrawing substituents. This appears so despite the varying structural and conjugative factors which may influence the energies of the lone-pair orbitals of the uncomplexed ligands.

Experimental Section

Preparation of Compounds. The complexes were prepared by the method of Connor[10] from the salt $[Et_4N^+][Cr(CO)_5Br^-]$, ca. 10–20% molar excess of the phosphine or sulfide, and $Et_3O^+BF_4^-$ in methylene chloride solution at room temperature. The halide starting material was prepared by the method of Abel.[11] The complexes were purified by sublimation onto a cold finger and chilled with dry ice–acetone. The Et_3P and Me_2S complexes were obtained as low-melting solids, mp 25–29 and 11–14 °C, respectively, while the others were obtained as oils.

The complexes could be easily and clearly characterized by their mass spectra, since the initial fragmentation is dominated by peak clusters corresponding to the successive loss of CO groups.[12] Peaks of mass number greater than the molecular ion could be assigned to $M(CO)_4L_2^+$, and the presence of $M(CO)_6^+$ could easily be detected. Traces of disubstituted product were found in the spectra of the phosphine complexes, while $Cr(CO)_6$ was found in the spectra of the divinyl sulfide and $(CH_3)(CH_2Cl)S$ derivatives.

Table IV lists the analytical data for the new complexes prepared (except for the divinyl sulfide complex), as well as the values of ν_{CO}. The infrared spectra were obtained on hexane solutions, using a Perkin-Elmer Model 247 spectrophotometer. An extra peak at 1980 cm^{-1} in the vinyl and chloromethyl derivatives indicated the presence of $Cr(CO)_6$.[13] A weak band at ca. 1910 cm^{-1} in many of the spectra is of unknown origin.

Measurement of Photoelectron Spectra. The spectra were obtained with a Perkin-Elmer Model PS-18 spectrometer, using the He I resonance line (21.22 eV). Since elevated temperatures were necessary for proper vapor pressures of the complexes investigated, a direct-inlet probe was used. The spectra were calibrated with Ar (15.76-eV line) and Xe (12.13-eV line) as internal standards. The IP values listed are the band maxima.

Registry No. $Cr(CO)_5(C_2H_5)_3P$, 21321-30-2; $Cr(CO)_5(C_2H_3)_3P$, 65338-52-5; $Cr(CO)_5(C_2H_5)_2S$, 60149-92-0; $Cr(CO)_5(CH_3)_2S$, 31172-83-5; $Cr(CO)_5(CH_3)(CH_2Cl)S$, 65338-63-8; $Cr(CO)_5(C_2H_3)_2S$, 65338-62-7; $(C_2H_5)_3P$, 554-70-1; $(C_2H_3)_3P$, 3746-01-8; $(CH_3)_2S$, 75-18-3; $(C_2H_5)_2S$, 352-93-2; $(C_2H_3)_2S$, 627-51-0; $(CH_3)(CH_2Cl)S$, 2373-51-5.

Supplementary Material Available: Figure showing the photoelectron spectra of the complexes (1 page). Ordering information is given on any current masthead page.

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Preparation of Dithiocarbamate Ligands Derived from Indole, Indoline, Carbazole, and Imidazole and Representative Transition-Element Complexes

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Received July 21, 1977

We recently reported the preparation of the pyrrolecarbodithioate ligand and selected transition-element complexes[1] exploiting a route first outlined by Trofimenko in the preparation of the 1-pyrazolecarbodithioate ligand.[2] This