In other words the rate constant should *decrease* with increasing nucleophile concentration. In addition k_{obsd} should increase with increasing nitrite concentration. This behavior was observed. For $[NO_2^-]$ fixed at 0.025 M, k_{obsd} decreases from 6.3 (at $[SCN^-] = 0.02\ M$) to 4.9 (at $[SCN^-] = 0.1\ M$). For $[NO_2^-] = 0.1\ M$, the k_{obsd} values are higher but still decrease with increasing $[SCN^-]$, from 10.1 ($[SCN^-] = 0.02\ M$) to 5.9 ($[SCN^-] = 0.1\ M$). The possibility that this rate decrease was the result of increasing ionic strength due to the SCN^- was ruled out on the basis of the following experiment. The kinetic data for $[NO_2^-] = 0.1\ M$ were collected at two ionic strengths, 0.25 M (data above) and 1.0 M (KNO_3). The higher ionic strength caused not a decrease but an increase in k_{obsd} of about 40%. Thus the decrease in rate with increasing $[SCN^-]$ cannot be an ionic strength effect.

We feel that our results are in good agreement with that predicted from the data of Blanck, *et al.*,[1] especially when small differences in ionic strength and temperature are considered. The conclusion is that the rates of ligand substitution on ferric myoglobin can be quantitatively predicted from a knowledge of aquation and anation rates. A species such as Y-Mb-L never becomes important during the reaction. For anation and aquation one expects the usual dissociative interchange mechanism to hold and the results for ligand substitution presented herein clearly support this.

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Registry No. Horse heart myoglobin, 12585-26-1; Fe^{3+}, 20074-52-6; SCN^-, 302-04-5; N_3^-, 14343-69-2; OCN^-, 661-20-1; NO_2^-, 14797-65-0; CN^-, 57-12-5.

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Photoelectron Spectra of the Rhenium Pentacarbonyl Halides

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HeI ultraviolet photoelectron spectroscopy (UPS) of the manganese pentacarbonyl halides $Mn(CO)_5X$ (X = Cl, Br, I) has recently received considerable attention.[2-5] From experimental[2,5] and theoretical[3,4] considerations it has been shown that, in contrast to the situation normally observed in transition metal complexes, the highest occupied molecular orbital is primarily of ligand character. The most recent interpretation of UPS is that of Lichtenberger, Sarapu, and Fenske, who proposed, partly on the basis of theoretical calculations, that the energy ordering of the four highest filled molecular orbitals is $X_\pi > X_\sigma > e(d_{xz}, d_{yz}) > b_2(d_{xy})$.[2] The X_π and X_σ levels are of symmetry e and a_1, respectively, but the X_π and X_σ notation will be used exclusively in this paper.

The present paper describes our investigations of the low-energy photoelectron spectra of the $Re(CO)_5X$ series. This study was of interest since UPS has been used in a relatively limited number of transition metal complexes with noncubic symmetry and since an interpretation of the electronic spectra of the $Mn(CO)_5X$ species has been based on the orbital ordering obtained from UPS results.[6] By contrasting the ionization potentials obtained for the Re series with those of the Mn complexes, we wished to determine the changes which take place in orbital structure with variation of the central metal atom and to see whether these data are consistent with previous interpretations. Our results now lead us to propose a new energy level ordering which we believe is appropriate for both the Mn and Re complexes.

Experimental Section

The rhenium pentacarbonyl halides were synthesized by methods analogous to those used to prepare the corresponding Mn complexes.[7,8] HeI spectra were recorded on a Vacuum Generators ESCA-2 photoelectron spectrometer operating at 35-MeV resolution. The iodide complex was sufficiently volatile to allow gas-phase spectra to be obtained at room temperature. For $Re(CO)_5Cl$ and $Re(CO)_5Br$ it was necessary to heat the ionization chamber to 70° before spectra could be obtained.

Results

The ultraviolet photoelectron spectra of the $Re(CO)_5X$ series are shown in Figure 1 for the critically important 8-12-eV region and compared with the results on the Mn analogs[2] in Table I. (In constructing Table I, the position of bands split by spin-orbit coupling is taken as the average of the two components.) For the purpose of the discussion which follows ionization potentials are labeled I-IV with the lowest ionization being I.

The $Re(CO)_5X$ spectra are characterized by several features which distinguish them from those of the Mn complexes. First, band II is seen for all X (Cl, Br, I) whereas it is not directly observed in $Mn(CO)_5I$. Second, band I, assigned as an ionization from a degenerate level on intensity grounds,[2] exhibits more pronounced spin-orbit splitting in the case of $Re(CO)_5I$ than in $Mn(CO)_5I$ and even shows splitting for $Re(CO)_5Br$ whereas none is seen in $Mn(CO)_5Br$. These results suggest that the highest occupied molecular orbital, which we assign as being primarily of halogen parentage (*vide infra*), has a not insignificant amount of metal character. The presence of metal character in this level would then increase the observed spin-orbit splitting since the spin-orbit coupling constant for Re is much larger than that of Mn (0.3 *vs.* 0.03 eV). An alternative explanation for the larger splitting in the Re complexes is that the X_π level is more nearly pure halogen in character than in the Mn species. Third, band III for $Re(CO)_5Br$ is split into two peaks separated by 0.12 eV while the chloride and iodide show no apparent splitting for this level. According to the arguments made above, band III, which is primarily of metal character (*vide infra*), should show some doublet splitting. Its absence in the chloride and iodide derivatives may result from changes in the amount of metal character due to halogen or carbonyl π mixing[2] or possibly from inductive changes in the effective charge on the metal, since the spin-orbit coupling

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(1) (a) University of Rochester. (b) Texas A&M University. (c) This research constitutes partial fulfillment of the Ph.D. degree requirements of J. L. C.

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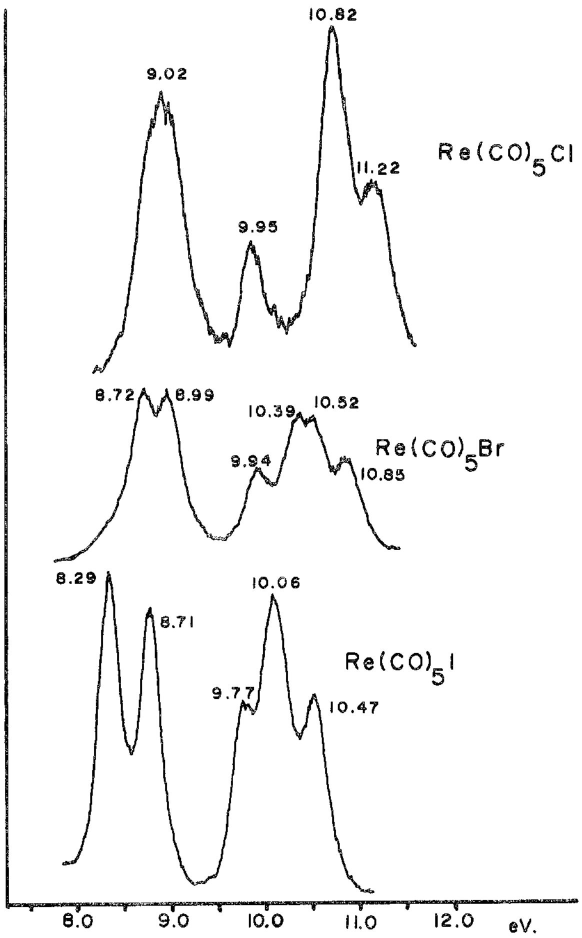

Figure 1. Ultraviolet photoelectron spectra of the metal d and halogen p regions for $Re(CO)_5X$.

Table I. Ionization Potentials of the Pentacarbonyl Halides of Mn and Re (eV)

Band	$Mn(CO)_5X^a$	$Re(CO)_5X^b$	Diff^c
		X = Cl	
I	8.94	9.02	0.08
II	9.56	9.95	0.39
III	10.56	10.82	0.26
IV	11.18	11.22	0.04
		X = Br	
I	8.86	8.86	0.0
II	9.56	9.94	0.38
III	10.11	10.46	0.35
IV	10.81	10.85	0.04
		X = I	
I	8.59	8.50	−0.09
II		9.77	
III	9.69	10.06	0.37
IV	10.44	10.47	0.03

[a] Reference 2. [b] This work. [c] IP(Re) − IP(Mn).

constant is dependent on this parameter. In any case, the question of the origin of the splitting of band III will not materially affect the remaining discussion.

Discussion

We propose that the photoelectron spectra are best interpreted assuming the level ordering $X_\pi > b_2 > e > X_\sigma$. This corresponds to an inversion of the positions of the nondegenerate b_2 and X_σ levels in the scheme suggested by Lichtenberger, Sarapu, and Fenske.[2] The basis for this conclusion comes from a comparison of the photoelectron data for the Mn and Re complexes with each other and with other halogen-containing compounds.

First, from Table I it can be seen that bands I and IV are functions of X only and are virtually independent of M while bands II and III shift to higher IP by *ca.* 0.4 eV as M changes from Mn to Re. A change of this magnitude is consistent with the first IP for Re being 0.4 eV greater than that of Mn and with the observation that Re metal IP's are shifted *ca.* +0.4 eV in compounds like $Re_2(CO)_{10}$[9] and $ReH(CO)_5$[10] compared to their Mn analogs. These correlations clearly pinpoint II and III as b_2 and e metal type levels and I and IV as ionizations from the X_π and X_σ orbitals.

Support for this assignment comes from the fact that band II varies least with X for both the Mn and Re series. This is precisely what is to be expected for the b_2 metal carbonyl level. This orbital is nonbonding with respect to the halogen and should change only slightly due to inductive effects as the halogen is changed. It should, however, be sensitive to the central metal atom as is shown by the IP data. Halogen levels, on the other hand, would be expected to vary as X is changed, as would the metal e orbital to some extent since it has the proper symmetry to mix with the X_π orbital. Band IV, which does vary with X, would thus seem to be a poor choice for the b_2 level on the basis of the data in Table I.

It should also be pointed out that the IP of II is in good agreement with energy values we estimate for the b_2 level. This was done by using electronic spectral work of Beach and Gray[11] which established that the $2t_{2u}$ π^* CO level in hexacarbonyl complexes is essentially invariant to the central metal. Their analysis placed the π^* level at a constant 23,400 ± 600 cm^{-1} for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$. Using this value and the energy of the $2t_{2g} \rightarrow 2t_{2u}$ transition for $Mn(CO)_6^+$ and $Re(CO)_6^+$ we predict the b_2 level to be at *ca.* 9.1 and 9.3 eV for the present Mn and Re complexes. These numbers are in reasonably good agreement with the observed trend in experimental IP's for band II.

Simple molecular orbital theory also helps in ordering the metal levels once it has been established that the highest filled level corresponds to the X_π level of e symmetry. To first order, on descending in symmetry from O_h to C_{4v}, the e_g orbitals are split by σ interactions while the t_{2g} level is split by π interactions. If we consider a $M(CO)_5X$ molecule with the X_π level above the initially unsplit b_2 and e metal levels, simple molecular orbital theory predicts that the e level should drop below the noninteracting b_2 level and not be above it; this is not an unreasonable explanation since the b_2 level should be unaffected by the X group.

We note that the assignments of Lichtenberger, *et al.*, require that bands III and IV correspond to metal levels. Accepting this assignment thus means either that a constant b_2-e ligand field separation exists for the Re series or that this separation decreases in the Mn complex in the order I > Br > Cl. Our assignment indicates that the b_2-e separation decreases in the order Cl > Br > I exactly as would be suggested by the spectrochemical series.

Further evidence for our ordering is gained by observing that the energy difference between bands I and II for the Re series is 0.90, 1.10, and 1.20 eV for X = Cl, Br, and I, respectively. This increasing energy difference is opposite to the decreasing X_π-X_σ separation which is generally seen in

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halogen compounds on going from Cl to Br to I (*e.g.*, CH_3X,[12] HX,[12] X_2[13]). Thus, our assignment of band IV as an ionization from the X level leads to a more acceptable X_π-X_σ separation with respect to the trend on variation of halogen.

We believe that our results and line of reasoning (applicable to both the Mn and Re complexes) clearly establish the ordering $X_\pi > b_2 > e > X_\sigma$ for the $M(CO)_5X$ molecules under discussion. The advantages of varying the metal as well as the ligand as an aid to interpreting photoelectron spectra of transition metal complexes have been clearly demonstrated.

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Registry No. $Re(CO)_5Cl$, 14099-01-5; $Re(CO)_5Br$, 14220-21-4; $Re(CO)_5I$, 13821-00-6.

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Tin-119m Mossbauer Spectra of Para-Substituted Dichlorotetraphenylporphinatotin(IV) Complexes

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In a previous report of the Mossbauer spectra of various tin complexes of phthalocyanine and tetraarylporphins,[1] Curran and O'Rourke indicated their inability to resolve a possible quadrupolar splitting in the spectra of four dichlorotetraarylporphinatotin(IV) compounds. We now wish to report the successful resolution of the quadrupolar splittings in seven such compounds including those studied by Curran and O'Rourke. The compounds are all derivatives of dichlorotetraphenylporphinatotin(IV), hereafter identified as Cl_2Sn-TPP, differing by various substitutions at the para positions of the four phenyl groups. The seven substituents studied were F, Cl, Br, CH_3, OCH_3, and i-C_3H_7, in addition to the H of the parent compound, and were prepared and characterized by previously reported methods.[2]

A representative spectrum clearly showing such a resolved splitting is shown in Figure 1 and a summary of all the ^{119m}Sn Mossbauer spectral parameters obtained at 80 K is given in Table I. All spectra were obtained with a $Ba^{119m}SnO_3$ source held at room temperature and the isomer shift (IS) values are reported with respect to a $BaSnO_3$ absorber at room temperature. The uncertainties indicated in parentheses for both the IS and the quadrupole splitting (QS) represent the 1σ confidence range for the precision of the evaluated parameters; we estimate the overall 1σ confidence level, including both uncertainties in the precision and the accuracy, to require the addition of 0.01 mm/sec to the stated numbers. The total count accumulation per data point for these spectra range from one to ten million and all compounds demonstrated a large resonance effect. Spectrometer calibration spectra were "time-sandwiched" about each sample spectrum and the expressed uncertainties are the pooled uncertainties of each sample spectrum and two calibration spectra. The spectral parameters were obtained with the aid of the PARLOR computer program[3] which assumes that the spectra represent independent lorentzian absorption curves on a parabolic base line.

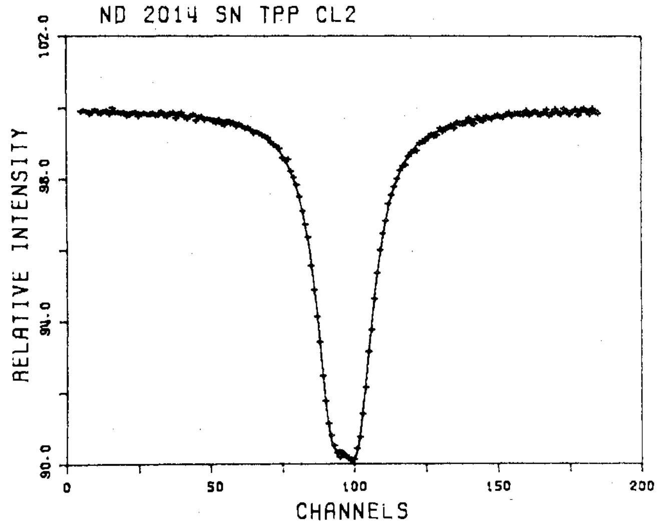

Figure 1. ^{119m}Sn Mossbauer spectrum of dichlorotetraphenylporphinatotin(IV), Cl_2SnTPP, at 80 K.

Table I. ^{119m}Sn Mossbauer Spectral Parameters of Para-Substituted Cl_2SnTPP

Compd	IS[a-c]	QS[a,b,d]	Area ratio[e]
$Cl_2SnT(p\text{-}i\text{-}C_3H_7)PP$	0.160 (0.010)	0.512 (0.012)	0.65
$Cl_2SnT(p\text{-}CH_3)PP$	0.153 (0.008)	0.592 (0.010)	0.77
Cl_2SnTPP	0.146 (0.007)	0.588 (0.008)	0.73
$Cl_2SnT(p\text{-}OCH_3)PP$	0.147 (0.008)	0.555 (0.010)	0.75
$Cl_2SnT(p\text{-}Br)PP$	0.147 (0.005)	0.659 (0.007)	0.80
$Cl_2SnT(p\text{-}Cl)PP$	0.154 (0.006)	0.642 (0.007)	0.87
$Cl_2SnT(p\text{-}F)PP$	0.165 (0.013)	0.463 (0.018)	0.60

[a] Isomer shift (with respect to $BaSnO_3$) and quadrupole splitting in mm/sec, defining the room-temperature parameters of our $(CH_3)_2$-SnF_2 calibration sample to be IS = 1.2455 mm/sec and QS = 4.4945 mm/sec. All spectra were recorded at 80 K. [b] Numbers in parentheses represent the *ca.* 68% confidence level in the precision. [c] Correlation index for the two wing positions taken to be +1.0 during calculation of σ. [d] Correlation index for the two wing positions taken to be 0.0 during calculation of σ. [e] Area of high-energy wing divided by area of low-energy wing.

The seven compounds clearly exhibit variations in the quadrupole splitting outside of the stated uncertainties in addition to more poorly defined variations in their isomer shifts. The presence of these resolvable splittings is somewhat surprising as the tin atom is bonded only to other atoms which all possess lone-pair electrons, a bonding situation which usually results in a singlet spectrum. Correlations of both spectral parameters (IS, QS) with the following empirical

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