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X-ray Photoelectron Spectra of Some Rhenium Halides

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Argon ion bombardment of some rhenium trihalides ReX_3 (X = Cl, Br, I) in a photoelectron spectrometer yielded lower valency rhenium halides. The presence of these new compounds was established on the basis of the destabilization of the $Re(4f_{5/2,7/2})$ spin–orbit component's binding energies and the relative decrease of the halogen spectral lines' intensities. A linear correlation between the Re(4f) binding energies for each series of rhenium halides and the oxidation number was observed. A correlation between the Re binding energies and the Re charges, calculated by the extended Hückel method, was noted.

Some rhenium compounds are used in supported heterogeneous catalyst. Previous XPS studies of several rhenium complexes dealt with the interaction between rhenium and the support.[1,2] The presence of any type of chemical interaction between the rhenium and the support as a result of reduction and chlorination treatments of the catalyst may be observed as changes in Re(4f) spin–orbit component binding energies. A considerable change in the valence band energy region is expected as a result of such interaction. Moreover, because of the numerous valencies which rhenium can have, it is important to investigate the relation between Re(4f) binding energies and the oxidation number. Such a relation could be very helpful in predicting the type of interaction between the rhenium compound and the support. In the case of rhenium trihalides (which are known as the lowest valency compounds prepared in this series except for ReI_2[3]), it was observed that under positive argon ion bombardment the Re(4f) binding energies decrease as the duration of sample exposure to argon ion increase. The decrease in binding energy is accompanied by a decrease of halogen spectral line intensity. So that such a process could be understood, a pure sample of each of the rhenium trihalides was studied separately. Two main criteria were considered. First, the relative change in the binding energy of Re(4f) spin–orbit components as compared to those of ReX_3 and Re(0) metal. Second, the ratio of the areas Re(4f)/Cl(2p) in $ReCl_3$, Re(4f)/Br(3d) in Re Br_3, and Re(4f)/I(4d) in ReI_3 were considered. The decrease in energy of the Re(4f) spin–orbit components signifies a decrease in the rhenium valency. This implies a decrease in the number of halogen atoms that are bonded to one rhenium atom. Such decrease in the number of the halogens should be consistent with the relative increase in the relative areas in each case.

Table I. Ionization Energies of Rhenium Halides (eV)

	Re						
compd	$4f_{7/2}$	$4f_{5/2}$	Cl(2p)	Br(3d)	$I(4d_{3/2},$	$_{5/2})$	ratio[a]
$ReCl_3$	43.3	45.6	199.4				2.0
$ReCl_2$	42.6	44.8	199.0				2.8
ReCl	41.6	43.8	198.9				6.0
$ReBr_3$	43.0	45.3		69.7			1.1
$ReBr_2$	42.2	44.5		69.3			1.9
ReBr	41.4	43.7		69.3			3.4
ReI_3	42.2	44.4			50.5	49.4	0.9
ReI_2	41.7	44.0				49.9	1.3
ReI	41.2	43.4				50.0	2.6
Re(0)	40.6	42.9					

[a] Ratio of the areas; see text.

Rhenium trichloride is known to exist as a dark red solid in the trinuclear cluster from $(ReCl_3)_3$. The XPS of this compound shows two distinct lines at 45.6 and 43.3 eV as shown in Figure 1a. These are assigned to the $Re(4f_{5/2})$, $Re(4f_{7/2})$, spin–orbit components, respectively. The full-width at half-maximum (fwhm) of this band is 4.5 eV. The chlorine 2p spectral line (shown in Figure 1a′) is at 199.4 eV, and the ratio of the areas Re(4f)/Cl(2p) is 2.0. Bombardment of a $ReCl_3$ sample by argon ions results in a decrease in the Re(4f) binding energies and a corresponding decrease in the Cl(2p) line intensity. Such a process indicates the possibility of reduction of $ReCl_3$ to lower valency state(s). Since low-valency rhenium chlorides such as $ReCl_2$ and ReCl have not been previously observed. It is of special interest to determine whether these compounds do in fact exist under appropriate experimental conditions. A $ReCl_3$ sample was introduced in the sample compartment and XPS spectra were recorded after argon ion bombardment for different durations. After bombardment by argon ions for 5 s, the Re(4f) spin–orbit lines were at 44.8 and 42.6 eV (Figure 1b), while the chlorine 2p was at 199.0 eV (Figure 1b′). The ratio of the areas of Re(4f)/Cl(2p) was 2.8. Further argon ion bombardment for a total of 40 s resulted in further changes in the Re(4f) binding energies at 43.8 and 41.6 eV (Figure 1c) while the Cl(2p) line remained relatively unchanged at 198.9 eV (Figure 1c′). However, the relative intensity of the Cl(2p) showed a substantial decrease, which resulted in an increase in Re(4f)/Cl(2p) area ratio to a value of 6.0. Further argon ion bombardment of the sample did not produce any change neither in the Re(4f), Cl(2P) binding energies nor in the relative areas. A comparison between the $Re(4f_{5/2})$, $Re(4f_{7/2})$ binding energies of the Re(0) metal at 42.9 and 40.6 eV and those of $ReCl_3$ shows an energy difference of ~3 eV for each spin–orbit component binding energy. This can be interpreted in terms of ~1 eV energy difference per oxidation number. In fact, it can be easily shown that the energy difference in the various states which results from the argon ion bombardment of $ReCl_3$ is of the order of ~1 eV. Moreover, the ratio of the areas of Re(4f)/Cl(2p) in the compounds $ReCl_3$:$ReCl_2$:ReCl were in the order $^1/_3$:$^1/_2$:1, respectively, where the denominator is the number of chlorine atoms directly bonded to rhenium. It is therefore concluded that 5-s argon ion bombardment results in the reduction of $ReCl_3$ to $ReCl_2$. Further bombardment of up to 40 s causes the reduction of $ReCl_2$ to ReCl. A plot of the Re(4f) spin–orbit energies vs. the oxidation number of rhenium chlorides (Figure 2) yields a linear relation. Since the fwhm of the Re(4f) band remains constant at 4.5 eV in each of the three states separately, it is concluded that we are dealing with one valency in each state. The simultaneous presence of mixed valency or binuclear structure results in broader fwhm for the Re(4f) band. When $ReBr_3$ and ReI_3

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(1) Shapiro, E. S., Aveav, V. I.; Antoshin, G. V.; Ryashentseva, M. A.; Minachev. Kh. M. *J. Catal.* **1978**, *55*, 402.

(2) Lawrence, S., Jr.; Jones, G. L.; Hercules, D. M. *Appl. Spectrosc.* **1980**, *34*, 624.

(3) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Interscience: New York, 1972; p 977.

0020-1669/82/1321-1523$01.25/0

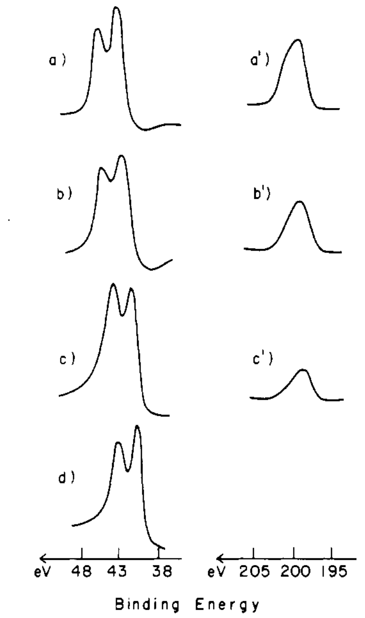

Figure 1. X-ray photoelectron spectra of Re(4f) and Cl(2p) of $ReCl_3$ at different intervals of argon ion bombardment: (a, a′) without argon ion bombardment; (b, b′) after 5 s; (c, c′) after 40 s; (d) as Re(0) metal.

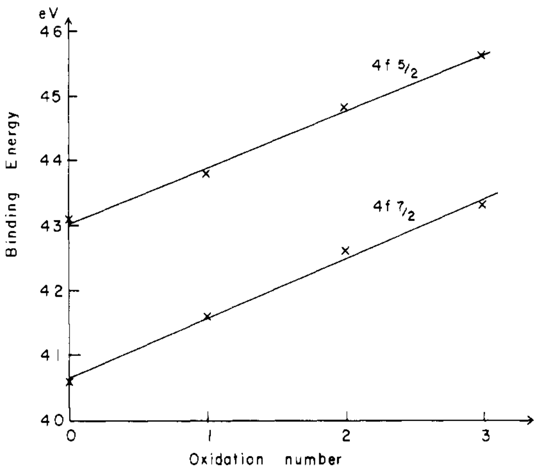

Figure 2. Plot of Re(4f) spin–orbit components binding energies vs. the oxidation number in rhenium chlorides.

were similarly treated, the results were identical with those observed for $ReCl_3$.

The Re(4f) spin–orbit components of rhenium tribromide are at 45.3 and 43.0 eV. These energies changed to 44.5 and 42.2 eV after 10 s of argon ion bombardment and to 43.7 and 41.1 eV when the bombardment continued for 90 s. The Br(3d) spectral line shows considerable decrease in intensity, while its binding energies remains almost constant at 69.7 eV. From the decrease in the Re(4f) binding energies and the ratio of the areas of Re(4f)/Br(3d) it is concluded that $ReBr_3$ is reduced to $ReBr_2$ and ReBr after 10 and 90 s of argon ion bombardment. The relevent data is presented in Table I.

For ReI_3 the spectral changes occured after 10 and 90 s, respectively. The results are shown in Table I. It is interesting to note here that the binding energy of the I(4d) which is very close to the Re(4f) spin–orbit components remains constant at 50.0 eV, while the $Re(4f_{5/2})$ decreased from 44.4 eV in ReI_3 to 43.4 eV in ReI, thus excluding the charging affect of the sample as responsible for the Re(4f) energy change.

Table II. Calculated Re Charges in ReX_n

	ReX	ReX_2	ReX_3		ReX	ReX_2	ReX_3
Cl	0.752	1.530	2.303	I	0.473	1.051	1.515
Br	0.650	1.354	2.024				

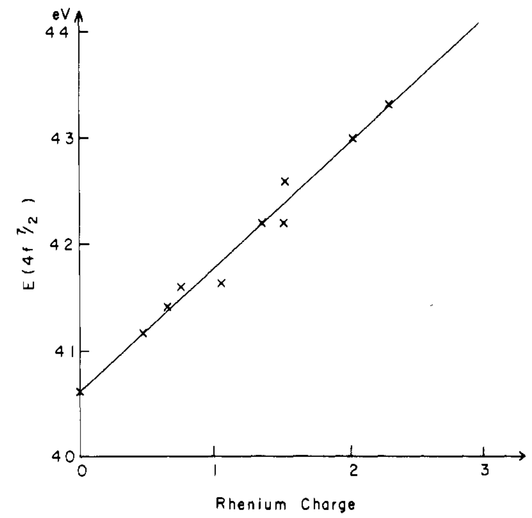

Figure 3. Plot of $Re(4f_{7/2})$ binding energies vs. the calculated rhenium charge in rhenium halides.

Extended Hückel molecular orbital calculations on ReX_n, where X = Cl, Br, I and $n = 1$–3, were undertaken in order to determine the extent of the influence of changing the halogen and the oxidation state on the Re charge. From the Re charge presented in Table II, the expected trends are noted. In every case the charges decrease in the order Cl > Br > I and also in the order $ReX_3 > ReX_2 > ReX$. Thus the decrease in ionization energies across the series Cl > Br > I and $ReX_3 > ReX_2 > ReX$ correlate with the calculated charges and yield a liner relation (Figure 3). The charges and the overlap populations from the molecular orbital calculations show increasing covalent character across the series Cl < Br < I. Furthermore, in all the calculations the highest occupied levels are essentially Re(5d) orbitals, and inside these, the next group of levels is made up mainly of halogen p orbitals.

In this study, it was possible to demonstrate that the bombardment of a rhenium trihalide sample by argon ions at different intervals enabled its reduction to Re(II) and Re(I) but not Re(0). It was observed that these low-valency rhenium halides are very stable in vacuum but not so in ambient atmosphere. The results of this study should be useful in the characterization of the nature of interaction between rhenium and the support of fresh catalysts and the same after treatment by reduction and chlorination at different temperatures.

Experimental Section

This work was carried out on a McPherson ESCA-36 spectrometer with an Mg Kα source at 1253.6 eV. A cryogenic pump in the sample chamber maintained a pressure of less than 10^{-8} torr. So that the sample-support interaction could be excluded, samples were mounted on aluminum or stainless-steel mesh. Their temperatures were approximately ambient. The sample was sputtered at normal incidence with 10 kV positive argon ions at a current of 20 $\mu A/cm^2$. The samples were all powders obtained from Pfaltz and Bauer, Inc., with very high purity. The measured binding energies of the compounds were based on the C(1s) at 285 eV.

Registry No. $ReCl_3$, 13569-63-6; $ReCl_2$, 18283-96-0; ReCl, 66411-56-1; $ReBr_3$, 13569-49-8; $ReBr_2$, 80409-97-8; ReBr, 80409-98-9; ReI_3, 15622-42-1; ReI_2, 39944-61-1; ReI, 15513-77-6.