Photoelectron Spectra of some Transition Metal Alkyls and Oxoalkyls

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The photoelectron spectra of WMe$_6$, ReMe$_6$, TaMe$_5$, ReOMe$_4$, and ReO(CH$_2$SiMe$_3$)$_4$ are presented. For the hexamethyls an ionization energy ordering of $3t_{1u} < 2a_{1g} < 2e_g$ is proposed.

The volatitity and simplicity of the transition metal permethyls WMe$_6$, ReMe$_6$, and TaMe$_5$ suggest that they are good candidates for study by photoelectron spectroscopy. A preliminary report of the spectra of TaMe$_5$ and WMe$_6$ has appeared.[1],† Here the assignments are discussed in more detail. Spectra of ReMe$_6$, ReOMe$_4$, and ReO(CH$_2$SiMe$_3$)$_4$ are also discussed.

EXPERIMENTAL

The compounds were prepared according to the literature methods [TaMe$_5$,[2] WMe$_6$,[3] ReMe$_6$,[4] ReOMe$_4$,[5] ReO(CH$_2$SiMe$_3$)$_4$ [5]] and the rhenium compounds were sublimed prior to spectral measurements. Samples of the Ta and W compounds were connected directly to the spectrometer. Initially the spectra were observed to change rapidly with time, usually with a falling intensity in the 10—11 eV region and a general sharpening up of features. This was assumed to be due to the presence of small amounts of volatile decomposition products. After *ca.* 10—15 min no further change was observed, and for the W compound the sample was run to complete exhaustion. With the Ta compound an explosion occurred after about half the sample had been used, and consequently some of the i.p. measurements reported are for rather small numbers of determinations.

He-I and He-II spectra of TaMe$_5$ and WMe$_6$ were obtained on a Perkin–Elmer PS16/18 spectrometer modified as described previously.[6] He-I spectra of ReMe$_6$ and ReO(CH$_2$SiMe$_3$)$_4$ were obtained on an unmodified PS16/18 instrument. The spectrum of ReOMe$_4$ was obtained on a spectrometer using He-I radiation and a 127 °C analyser combined with a variable retarding field.[7]

The binary metal alkyls were so volatile that the samples were held in a bath (*ca.* −10 to 0 °C) while the sample was bled into the spectrometer. ReOMe$_4$ held at room temperature and ReO(CH$_2$SiMe$_3$)$_4$ was heated to *ca.* 63 °C.

It should be noted that during the course of these investigations several serious explosions occurred.[8] *Extreme caution is recommended in the handling of these compounds.*

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† In this preliminary report the figure captions were interchanged by a printing error.

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RESULTS

The spectra are presented in Figures 1—4 and ionization energies (i.e.) given in the Table.

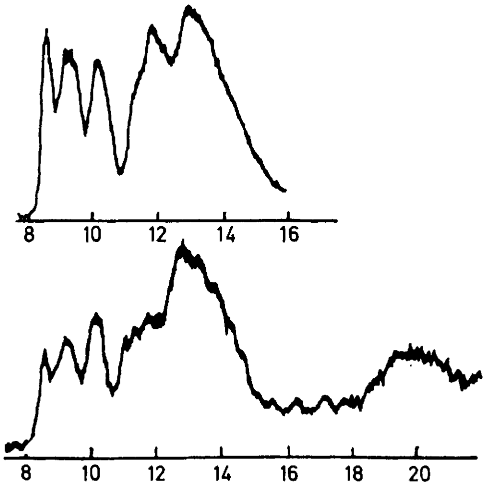

FIGURE 1 He-I and He-II photoelectron spectra of WMe_6

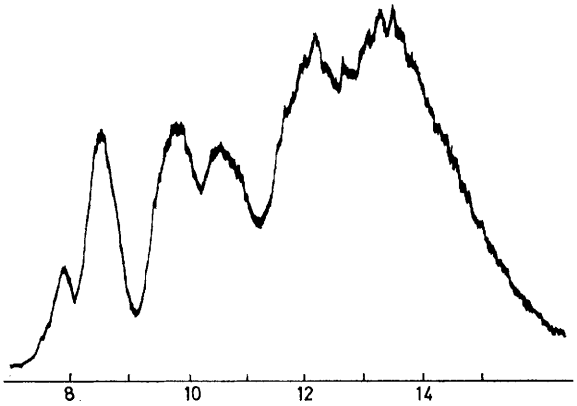

FIGURE 2 He-I photoelectron spectrum of $ReMe_6$

DISCUSSION

Examination of the spectra of these compounds suggests that the assignment and interpretation of the photoelectron bands is by no means straightforward. However we can arrive at a preferred assignment which we shall attempt to justify below. The procedure used for each compound is first, to predict the number of ionizations bands we can reasonably expect and then to assign the spectrum using such criteria as ionization

TABLE 1

Ionization energy data (eV) for $TaMe_5$, WMe_6, $ReMe_6$, $ReOMe_4$, and $ReO(CH_2SiMe_3)_4$

$TaMe_5$	WMe_6	$ReMe_6$	$ReOMe_4$	$ReO(CH_2SiMe_3)_4$
		7.89 (3)	8.86	8.00 (3)
8.83 (2)	8.59 (2)	8.47 (3)	9.5	8.46 (2)
9.25 (3)	9.33 (3)	9.77 (3)	9.95	8.93 (2)
10.10 *	10.17	10.48		
11.14	11.55 (sh)			10.2
12.07	11.97	12.2	13.0	12.9
13.51	13.14	13.4		
	20.8			

* 4 Determinations only (see text). The quantities in parentheses are standard deviations; where this is not given the precision is better than ±0.05 eV for sharp bands and *ca.* 0.1 eV for broad bands.

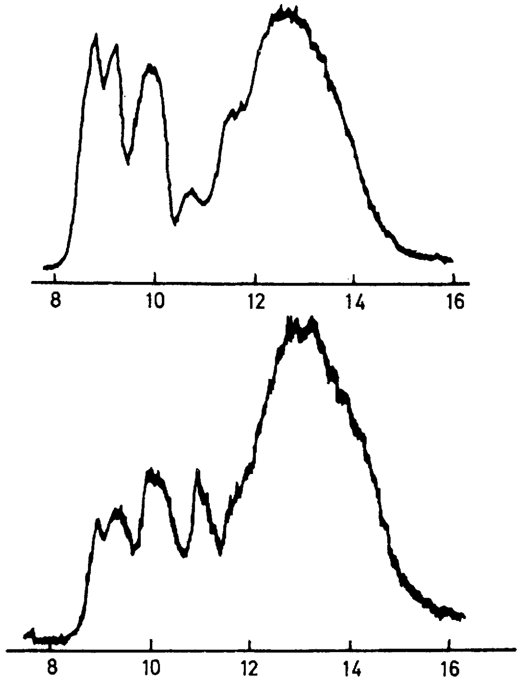

FIGURE 3 He-I and He-II photoelectron spectra of $TaMe_5$

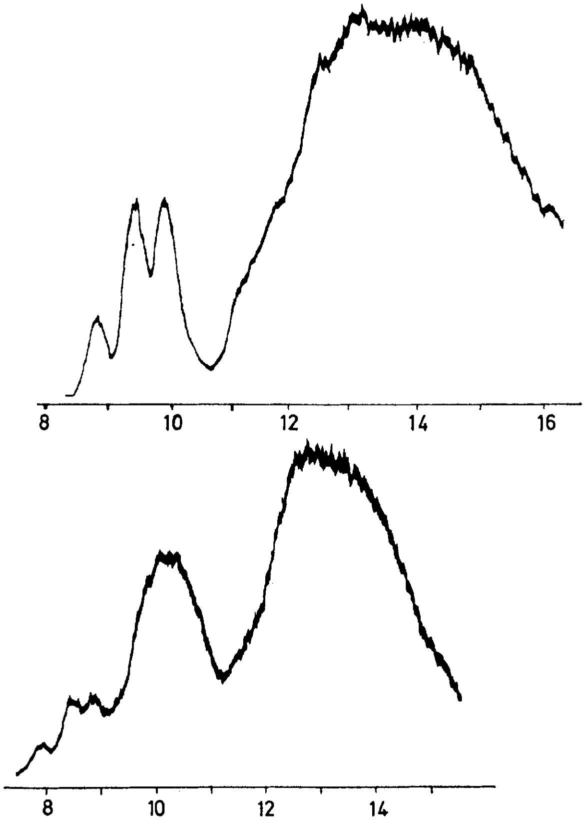

FIGURE 4 He-I photoelectron spectra of $ReOMe_4$ and $ReO(CH_2SiMe_3)_4$

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energies, band intensities, and comparison with similar compounds.

Ionization from *e* or *t* orbitals may lead to such a large Jahn–Teller instability of the molecular ion that more than one ionization band is observed for ionization from this class of orbital. Although effects of this type are well documented for tetrahedral alkyls [9,10] little analogous evidence is available in the rather different case of octahedral complexes. However for metal hexafluorides [11,12] and hexadialkylamides [13] no evidence for substantial (>0.3 eV) Jahn–Teller splitting has been found. Spin-orbit coupling can also give rise to more than one band on ionizing from these degenerate orbitals; however the spin-orbit coupling constants for the tree tungsten ($\xi_{5d} = 0.257\,7$ eV) and rhenium ($\zeta_{5d} = 0.281\,9$ eV) atoms [14] are too small to cause substantial splitting except for ionization from orbitals localized mainly on the metal atom.

A convenient way of constructing a molecular orbital description of this type of molecule is to use localized bond orbitals as a basis set. This approach has been used to assign the photoelectron spectra of other metal alkyls [9,10] and will be followed here.

Hexamethyltungsten.—If the WC_6 framework is taken to be of O_h symmetry [1] the six σ_{W-C} orbitals transform as $a_{1g} + t_{1u} + e_g$. The further assumption of local cylindrical symmetry for the CH_3 groups allows classification of the eighteen σ_{C-H} orbitals as $t_{1g} + t_{2g} + 2 \times t_{1u} + t_{2u} + a_{1g} + e_g$. So long as interactions between adjacent bond orbitals are stronger than those between more distant pairs of bond orbitals we may divide the σ_{C-H} orbitals into two groups namely $\sigma_{C(2s)-H}$ comprising a_{1g}, e_g and $1t_{1u}$ and $\sigma_{C(2p)-H}$ comprising t_{1g}, t_{2g}, t_{2u}, and $2t_{1u}$. By comparison with simple methyl compounds the former group will lie at 7—10 eV lower energy than the other. The transformation properties of the metal valence orbitals in this symmetry indicate the possible metal atomic orbital contributions to the molecular orbitals. They are $5d$-$e_g + t_{2g}$, $6s$-a_{1g} and $6p$-t_{1u}.

The photoelectron spectrum of WMe_6 (Figure 1) may be divided into three regions. From considerations of atomic ionization energies, comparison with the spectra of other alkyls [9,10] and dialkylamides,[13] the ionization region below 11 eV can be assigned to ionization from the σ_{W-C} bonding orbitals, that from 11 to 16 eV to ionization from $\sigma_{C(2p)-H}$ bonding orbitals and that at 20.8 eV to ionization from $\sigma_{C(2s)-H}$ bonding orbitals.

In view of the arguments presented above we propose that the first three bands must be assigned to ionization from the σ_{M-C} orbitals. The intensities of these bands are clearly not compatible with the 1 : 2 : 3 degeneracy ratio of the orbitals. Examination of the He-I spectra of several methyls [9] and dialkylamides [13] shows that the ionization intensities from M–C or M–N bonding orbitals are quite sensitive to the nature of the M orbitals and are generally rather weak in comparison with those from C–H bonding orbitals. Thus in Group 4B tetramethyls [9] the intensity of the ionization band corresponding to the M(*np*)–C bonding t_2 orbitals varies between *ca.* 70% (Ge) and 34% (Pb) of that expected, on degeneracy grounds, from the intensities of the C–H ionizations. For dimethylcadmium and dimethylmercury, where some inner *d* orbital contribution is probable, the equivalent figures are 80 and 90% respectively.[15] Participation by *d* orbitals appears to increase the intensity substantially, at least for the corresponding M–N bonding orbitals in tetrakisdimethylamido-compounds. Examination of the spectra [13] shows that these bands are approximately twice as intense in compounds of Ti, Zr, and Hf as in the corresponding Group 4B compounds.

Evidence is also available from the variation of band intensities on changing the photon source from He-I to He-II. Examination of the spectra of a number of metal complexes [6,16,17] shows that bands associated with ionization from orbitals with large metal *d* character increase substantially relative to those with mainly C $2p$ character on increasing the photon energy in this way. However the magnitude of this effect decreases substantially from first to third row transition elements. Bands from orbitals with *np* character where $n > 2$ in general decrease in intensity relative to carbon $2p$ bands.[18] Little information is available on the ionization intensity behaviour of orbitals with $6s$ character on changing the photon source though in mercury(II) halides the intensity of the σ_g ionization is believed to be essentially constant.[19]

Even with these guidelines, assignment is difficult as the bands in the spectrum of WMe_6 overlap so that their relative intensities cannot be determined accurately. Within the first three bands band 3 has a substantial increase in intensity in the He-II spectrum relative to bands 1 and 2 and stays roughly constant * relative to the larger C–H band (13.14 eV). For these reasons we assign band 3 to the e_g ionization. Since W $6p$ must lie higher than W $6s$, t_{1u} is expected to ionize before a_{1g}. The sharpness of band 1 suggests small bonding character in the corresponding orbital which also fits with assignment of this band to ionization from the t_{1u} orbital. The intensity of band 1 is low in the He-I spectrum for

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* There may be a slight decrease but this depends on how the band intensities are assessed.

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ionization from a triply degenerate orbital but this is reasonable for a m.o. formed mainly from C $2p$ with a small admixture of W $6p$ a.o., as is the decrease in intensity in the He-II spectrum. Band 2 is consequently assigned to the a_{1g} ionization. If this is the correct assignment, the surprising features are the high intensity of band 2 in the He-I spectrum, and the breadth, when compared with other ionization bands from orbitals with s-character [9,14,20,21] which are rather weak and sharp. However bands of this type in other methyls are noticeably less sharp than in halides or oxides. We find greater inconsistencies in alternative assignments and prefer the ionization energy order $3t_{1u} < 2a_{1g} < 2e_g$ for these $\sigma_{\mathrm{M-C}}$ orbitals.

The bands in the region 11—16 eV which have been assigned to ionization from $\sigma_{\mathrm{C(2}p\mathrm{)-H}}$ orbitals (t_{1g}, t_{2u}, $2t_{1u}$, t_{2g}) show substantial splitting similar to that found for neopentane.[9] This is probably due to considerable steric compression of the methyl groups. Band 4 (11.97 eV) drops in intensity relative to band 5 (13.14 eV) on changing from He-I to He-II radiation. The intensity change on band 4 is rather unexpected since both this and band 5 are assigned as mainly C–H bonding in character. Band 4 probably corresponds to the orbital set with maximum H–H antibonding interaction between adjacent CH_3 groups, t_{1g} in full O_h symmetry. Examination of the He-I and He-II spectra of neopentane [9,21] shows that here also the ionization intensity of the orbital with maximum H–H antibonding character, t_1 in T_d, decreases markedly from He-I to He-II excitation. The common cause could be a high degree of H(1s) localization of these orbitals.

Finally, we note that the ionization energy of the $\sigma_{\mathrm{C(2}s\mathrm{)-H}}$ bonding orbital set (20.8 eV) lies between the corresponding ionizations of CH_3Br (19.9 eV) and CH_3Cl (21.5 eV) (12).

Hexamethylrhenium.—E.s.r. studies suggest that $ReMe_6$ has a distorted octahedral geometry in solution:[22] the distortion, it appears, is not caused by solvent coordination. The photoelectron spectrum of $ReMe_6$ closely resembles that of WMe_6 but has one extra band at low ionization energy (7.98 eV) which may be assigned to ionization of the one 'd-electron'. The ground state $^2T_{2g}$ is expected to be split by spin-orbit coupling into $^2U'$ and $^2E''$ separated by approximately kT at room temperature. The asymmetry of the leading edge of the first ionization band may be due to ionization of the thermally populated $^2E''$ state of the molecule. In view of the similarity to WMe_6 the distortion from octahedral geometry appears small and not significant as far as the number of photoelectron bands is concerned. We therefore assign the bands by analogy with WMe_6. That the bands are broader and less well resolved in $ReMe_6$ may be due to exchange coupling of the hole in the M–C bonding orbital set with the unpaired d-electron. There is an irregular shift in ionization energy of the three M–C ionization bands on passing from WMe_6 to $ReMe_6$; the t_{1u} ionization decreases in energy (8.59 eV W; 8.47 eV Re) while the a_{1g} and e_g ionizations increase in energy (9.33, 10.17 eV W; 9.77 and 10.48 eV Re). This indicates a lower $6s$ and $5d$ orbital energy in Re and a better M–C interaction on the whole. The reverse shift for the t_{1u} ionization could be the result of a greater interaction with the t_{1u} C–H bonding set as the M–C distance decreases.

Pentamethyltantalum.—If we assume D_{3h} symmetry for $TaMe_5$ we find that the M–C bonding orbitals transform as $2 \times a_1' + a_2'' + e'$. The metal orbitals transform as follows: d-$a_1' + e' + e''$, s-a_1', p-$a_2'' + e'$. Four bands in the region of the spectrum of $TaMe_5$ below 11.5 eV are assigned to ionization from the M–C bonding orbitals. Again intensity criteria lead to no clearcut assignment. Band 1 is the least intense in the He-II spectrum and by analogy with WMe_6 is assigned to the a_2'' orbitals which can only have a metal p-contribution. Band 4 shows an intensity increase, relative to the main C–H region which fits with none of the established behaviour described above. The intensity of bands 2 and 3 in the He-I spectra leads us to suppose that they have substantial metal d-character therefore we propose the ordering of ionization energies $a_2'' < a_1' < e' < a_1'$.

The shoulder at 12.1 eV in the C–H bonding region shows a similar change in intensity on passing from He-I to He-II as does the band at 12.0 eV in the spectrum of WMe_6. This band occurs over a similar i.e. range but shows less structure than in WMe_6. This is compatible with the lower symmetry of $TaMe_5$.

Tetramethyl(oxo)rhenium.—We assume C_{4v} symmetry for this molecule in the gas phase. Again it is convenient to use localized bonding orbitals as a basis set. The metal–carbon bonds transform as $a_1 + b_1 + e$. Though there are metal d-orbitals which on symmetry grounds can contribute to these bonding orbitals it is likely that the contribution of the e symmetry pair, d_{xz}, d_{yz}, is small. Our grounds for suggesting this are that if the metal atom lies in the square of the four carbon atoms the overlap between the methyl σ-hybrid orbitals and the $d_{xz}\, d_{yz}$ orbitals is zero: the most plausible structure is that in which the metal lies above the square, but not sufficiently out of plane to make the overlap large. The metal d_{xz} and d_{yz} orbitals are expected to have strong interaction with the oxygen $p\pi$ orbitals. The antibonding interaction with the O2$p\pi$ levels is likely to raise the $e(\mathrm{C}2_p)$ levels. We therefore suggest that the $\sigma_{\mathrm{M-C}}$ e orbital lies above the a_1 and b_1 orbitals and has the lowest ionization energy. As the metal b_2 orbital is the only one which lacks a near neighbour ligand set to interact with, it seems a likely candidate for occupation by the d-electron. On electronegativity grounds and by comparison with other oxo-group spectra [23] we predict that the M–O π and σ orbitals will ionize in the same region as the $\sigma_{\mathrm{C-H}}$ orbitals.

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Our interpretation of the spectrum is as follows. The first band (8.86 eV) is assigned to ionization of the *d*-electron. There are two bands in the region where we would expect the three σ_{M-C} ionizations (9.5, 9.95 eV). Thus there must either be overlapping bands or one ionization is concealed under the structure which commences at 11.0 eV. We consider the latter hypothesis the more probable partly because of the clean profile of the two bands but also by comparison with ionization energy data of $ReMe_6$. $ReMe_6$ has a first i.p. of 7.89 eV whereas that of $ReOMe_4$ is significantly higher, 8.86 eV. This is readily explained by proposing that the inductive effect of the oxo-group is greater than that of two methyl groups. One would expect a similar effect on the M–C bonding orbitals. The highest i.p. found for these in $ReMe_6$ is 10.48 eV therefore a σ_{M-C} ionization for $ReOMe_4$ of energy >11.0 eV is reasonable. We therefore propose the ionization energy ordering $e < b_1 < a_1$. We note that again band intensity is a poor indicator of orbital degeneracy; on the above arguments it is reasonable that the b_1 orbital should have much more *d* character than the *e* orbitals.

There are no features in the broad band between 11 and 16 eV which lead to any suggestions as to the region of the M–O π and σ ionizations.

Oxotetrakis(trimethylsilylmethyl)rhenium.—The spectrum of $ReO(CH_2SiMe_3)_4$ (Figure 4) is readily assigned by comparison with that of $ReOMe_4$ and other trimethylsilylmethyl compounds.[11] The first band (8.00 eV) is assigned to a metal *d* ionization, bands 2 and 3 (8.46 and 8.93 eV) to ionization from σ_{M-C} bonding orbitals, and the band at 10.2 eV occurs in the region characteristic of Si–C bonding orbitals. The band at 11–16 eV is again presumably dominated by ionization of electrons localized in C–H bonding regions.

Conclusions.—The above assignments are consistent with a view of the metal–carbon bonding in transition metal alkyls in which the major metal atom component comes from the valence *d* orbitals. This parallels the evidence from photoelectron spectra on oxides and halides of the early transition elements. For the hexamethyls the breadth of the band assigned as a_{1g} also suggests appreciable binding contribution from W or Re 6*s* orbitals, as does the sensitivity of the i.e. to the nature of the metal.

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