The Photoelectron Spectra of Hexamethyltungsten and Pentamethyltantalum

By Lee Galyer and Geoffrey Wilkinson
(*Inorganic Chemistry Laboratories, Imperial College, London* SW7 2AY)
and D. Robert Lloyd*
(*Chemistry Department, University of Birmingham, P.O. Box* 363, *Birmingham* B15 2TT)

Summary The He I and He II photoelectron spectra of an authentic sample of hexamethyltungsten and of pentamethyltantalum are consistent with octahedral symmetry for the former and D_{3h} symmetry for the latter; the metal-to-carbon bonding appears to be mainly *d* and *s* in character with a little *p* contribution, and there is evidence for steric interaction between the methyl groups of WMe_6.

FOLLOWING a preliminary note,[1] later supplemented with details,[2] Cradock and Savage[3] reported the He I photoelectron spectrum of what they believed to be hexamethyltungsten. The He I (21.2 eV) and He II (40·8 eV) spectra (Figure 1) of the authentic material, synthesised by a new route,[4] are so different from the report of Cradock and Savage that we conclude that their spectrum is that of a different compound.

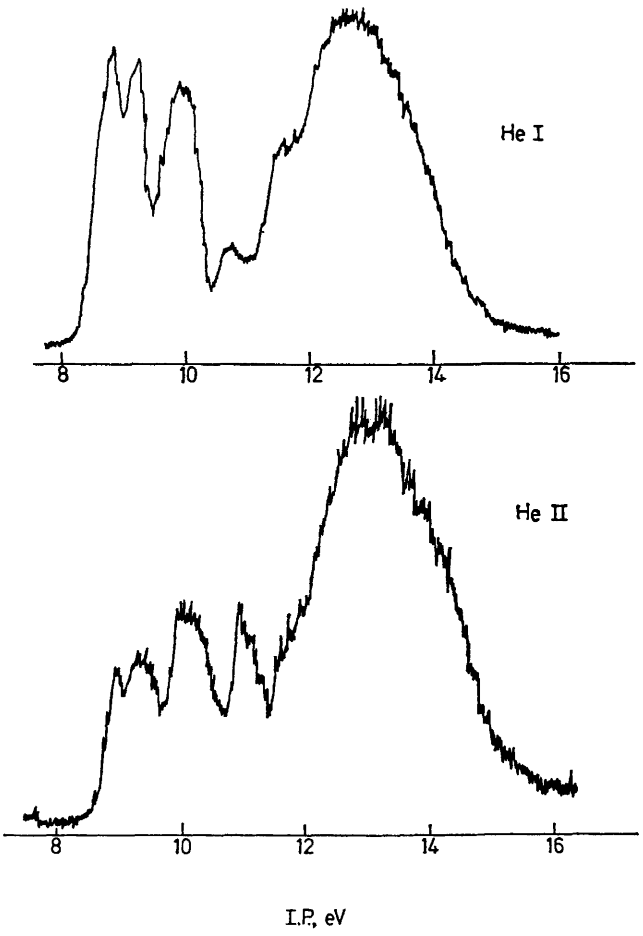

FIGURE 1. Photoelectron spectra of hexamethyltungsten, using He I (21·2 eV) and He II (40·8 eV) radiation.

By consideration of atomic ionization potentials and comparison with spectra of other methyls[5]† and dialkylamides[6] the ionization region below 11 eV can be assigned to W–C bonding orbitals and that from 11 to 16 eV to C(2*p*)–H bonding orbitals. The band at 21 eV in the He II spectrum can be assigned to C(2*s*)–H bonding orbitals. The spectra are fully consistent with an octahedral WC_6 skeleton. Three distinct ionizations from W–C bonding orbitals are observed as expected for a_{1g}, e_g, and t_{1u} orbitals in O_h symmetry. The substantial splitting of the methyl C–H bonding region can also be rationalized by octahedral symmetry where there are only four distinct sets, t_{1g}, t_{2g}, t_{1u}, and t_{2u}. The splitting indicates that there is considerable steric compression of the methyl groups as in neopentane.[5]

Detailed analyses, and comparison with other species, will be presented later; here we note that increase of intensity of bands in the He II spectrum can be associated with metal *d* character[7] and that our analysis leads to the assignment of bands 1, 2, and 3 as t_{1u}, a_{1g}, and e_g respectively.

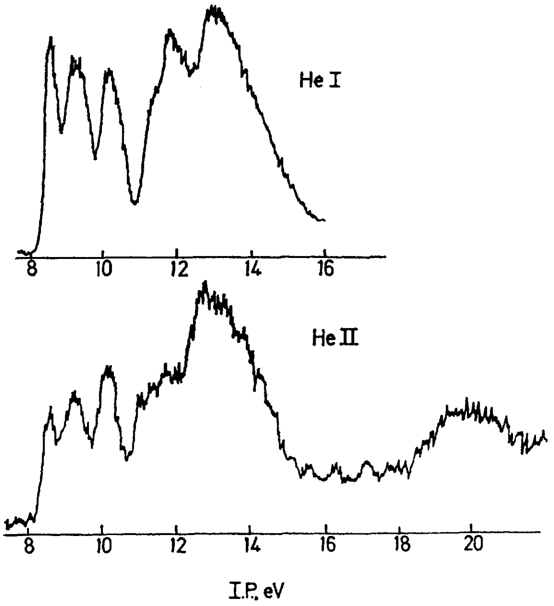

FIGURE 2. Photoelectron spectra of pentamethyltantalum, using He I (21·2 eV) and He II (40·8 eV) radiation.

For pentamethyltantalum[8] (Figure 2) there are four bands in the M–C bonding region which correspond to orbital $1a'_1$, a_2'', e', and $2a_1'$ of D_{3h} symmetry, as expected. All of these can have 5*d* character except a_2'', which can only have 6*p* metal character. In contrast to WMe_6, the lower symmetry leads to a smearing out in the methyl C–H bonding region and only one band of indistinct structure occurs, though the overall width is similar to that in WMe_6.

For both $TaMe_5$ and WMe_6 there is evidence from the intensity changes in the spectra for a large contribution to the bonding from 5*d* orbitals. In WMe_6 the breadth of the a_{1g} ionization and sharpness of the t_{1u} ionization suggest that there is substantial 6*s* character but little 6*p* character in the bonding. A classical 'd^2sp^3 hybrid' does not seem an appropriate description. Because of symmetry-allowed *s*–*d* and *p*–*d* mixing in $TaMe_5$, detailed analysis is not possible but there seems to be no reason for the bonding to be greatly different from that in WMe_6. The i.p. of the

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† Spectra of $ReOMe_4$ and $ReMe_6$ have also been obtained in collaboration with Dr. J. Green, Inorganic Chemistry Laboratories, Oxford.

C(2s)–H bonding orbital group, 20·8 eV, is intermediate between the i.p. of the corresponding orbitals in MeBr and MeCl;[9] contrary to earlier deductions[3] it seems that the electronegativity of W^{VI} is probably quite high.

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[1] A. J. Shortland and G. Wilkinson, *Chem. Comm.*, 1972, 318.

[2] A. J. Shortland and G. Wilkinson, *J.C.S. Dalton*, 1973, 872.

[3] S. Cradock and W. Savage, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 753.

[4] L. Galyer, K. Mertis, and G. Wilkinson, *J. Organometallic Chem.*, 1975, **85**, C37.

[5] S. Evans, J. C. Green, P. J. Joachim, A. F. Orchard, D. W. Turner, and J. P. Maier, *J.C.S. Faraday II*, 1972, **68**, 905; A. E. Jonas, G. K. Schweitzer, F. A. Grimm, and T. A. Carlson, *J. Electron. Spectroscopy*, 1972, **1**, 29; H. Bock and B. G. Ramsey, *Angew. Chem. Internat. Edn.*, 1973, **12**, 734; J. H. D. Eland, *Internat. J. Mass Spectrometry Ion Phys.*, 1970, **4**, 37.

[6] S. G. Gibbons, M. F. Lappert, J. B. Pedley, and G. J. Sharp, *J.C.S. Dalton*, 1975, **72**.

[7] M. F. Guest, I. H. Hillier, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, 1975, **29**, 113.

[8] R. R. Schrock and P. Meakin, *J. Amer. Chem. Soc.*, 1974, **96**, 5288.

[9] A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, *Phil. Trans. Roy. Soc. A*, 1970, **268**, 59.