December, 1982]

Bull. Chem. Soc. Jpn., 55, 3757—3759 (1982) 3757

UV Photoelectron Spectroscopic Investigation and the DV-Xα MO Calculation of Tetrakis(2-methyl-2-propanethiolato)molybdenum(IV)

Masao TAKAHASHI,* Iwao WATANABE, Shigero IKEDA, Masato KAMATA,† and Sei OTSUKA†
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560
†Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

(Received April 15, 1982)

Helium(I) ultraviolet photoelectron spectrum is reported for the compound $Mo(t\text{-}BuS)_4$. The observed spectrum is interpreted by means of DV-Xα MO calculations on the model compounds $Mo(SH)_4$ and $Mo(SMe)_4$. The UV photoelectron spectrum of $Mo(t\text{-}BuS)_4$ exhibits a low ionization potential band (IP=6.43 eV) which corresponds to ionization of mainly Mo4d$_{z^2}$ electron of A$_1$ representation. This molecular orbital has also bonding character between Mo4d and S3d.

Currently thiolatomolybdenum complexes due to their possible implication in redox-active molybdoenzymes are receiving considerable attention. The homoleptic tetrakis(thiolato)molybdenum(IV) compound and products derived therefrom were reported recently.[1,2] The electronic structures of molybdenum compounds have been investigated by use of X-ray and UV photoelectron spectroscopy (XPS and UPS).[3,4] The UPS is especially useful for the study of the valence orbitals in a molecule.

Recently the discrete-variational(DV)-Xα method has been shown to be useful for evaluating electron binding energies and studying electronic structures, and applied for the interpretation of photoelectron spectroscopic data of various materials.[5,6]

The $Mo(t\text{-}BuS)_4$ compound exhibits outstanding reactivity toward various reagents. In this paper we report the study on its electronic structure by using UPS and by performing the DV-Xα MO calculation.

Experimental

Materials. The compound, $Mo(t\text{-}BuS)_4$, was prepared and purified as described elsewhere.[1] This compound is sensitive to air and moisture and sublimes at 343 K (0.13 Pa). It was preserved under a nitrogen atmosphere until UPS measurements. The compounds, 2-methyl-2-propanethiol, di-*t*-butyl disulfide and 2-methyl-1-propene, were obtained commercially.

UPS Measurements. The He(I) photoelectron spectrometer used was constructed by one of the authors (I.W.). The spectrometer was controlled by a mini-computer so that the effect of energy drift of the spectrometer during the measurement was completely compensated by a real-time energy calibration technique.

The sample, $Mo(t\text{-}BuS)_4$, seemed to be liable to decomposition on heating, so UV photoelectron spectra for its expected decomposition products, *i.e.*, 2-methyl-2-propanethiol, 2-methyl-1-propene, and di-*t*-butyl disulfide, were also measured, and they were found to be identical with the spectra reported[7-9] (a, b, and c in Fig. 2 respectively). When the sample, $Mo(t\text{-}BuS)_4$, was heated to 340 K in a glass tube at the distance of 30 cm from the ionization chamber with an electric heater to obtain a sufficient vapor pressure for the measurement, the observed spectrum was that for the mixture of the above mentioned decomposition products. Therefore the ionization chamber as shown in Fig. 1 was necessary. On the wall of the ionization chamber two metal-film resistors (C in Fig. 1) and a calibrated thermistor (B) were fixed with aluminum tapes. An alternating current supplied to the resistors heated the ionization chamber, the temperature of which was measured by the thermistor. The magnetic field produced by the a.c. current caused neither peak shift nor peak broadening.

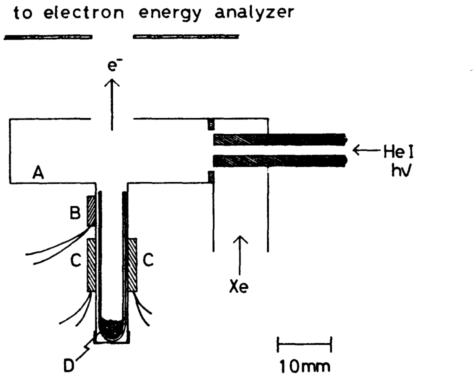

Fig. 1. Schematic drawing of ionization chamber. A) ionization chamber made of 0.2 mm thick copper sheet, B) thermistor, C) metal-film resistors, D) solid samples in a glass tube.

It was necessary to keep the temperature of the ionization chamber as low as possible in order to minimize the sample decomposition. The measurements were performed at 331$\pm$2 K, *i.e.*, about 10 K lower than the temperature at which the sublimation of $Mo(t\text{-}BuS)_4$ was noticeable. Because of the low vapor pressure at that temperature, the spectral data were accumulated for 2 d to get a satisfactory spectrum.

The ionization energy scale was calibrated with xenon used as an internal standard (IP=12.130 eV). Spectral resolution defined by the full width at half-maximum (FWHM) of the $^2P_{3/2}$ xenon peak was less than 30 meV. All ionization energies were read at the maximum of each peak as vertical ionization potential.

Computations. The DV-Xα method used was described in detail elsewhere.[10,11] Molecular orbital energies were calculated by employing models of $Mo(SH)_4$ and $Mo(SMe)_4$ for $Mo(t\text{-}BuS)_4$, and that of $Mo(NH_2)_4$ for $Mo(NMe_2)_4$. Each model has D_{2d} symmetry. Numerically generated atomic basis functions (1s-5p for Mo, 1s-3d for S, 1s-2p for C and N, and 1s for H) were used to expand the molecular orbitals. The bond distances and angles used for the calculations were taken from the results of X-ray crystallography for $Mo(t\text{-}BuS)_4$[1] and $Mo(NMe_2)_4$,[12] except that S–H, C–H, and N–H bond distances were taken to be 0.1336, 0.1090, and 0.1022 nm respectively. In the compound, $Mo(t\text{-}BuS)_4$, the MoS_4 skeleton has nearly perfect D_{2d} symmetry, while in $Mo(NMe_2)_4$, having exact D_{2d} symmetry as a whole, the MoN_4 moiety has almost perfect T_d symmetry. Thus we have chosen the

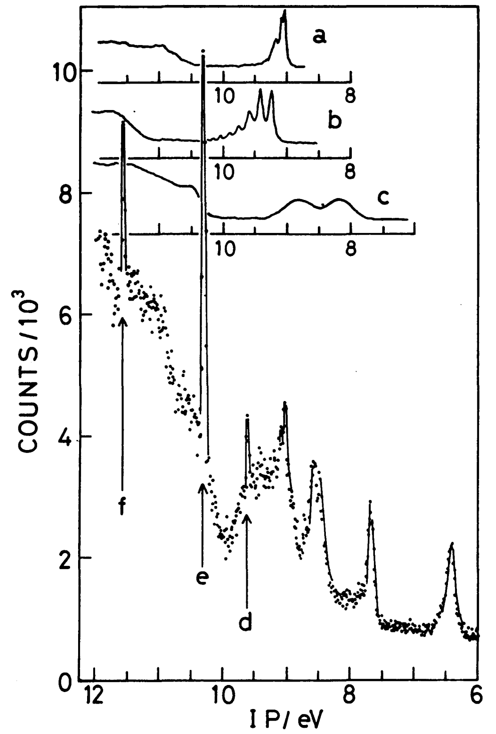

Fig. 2. He(I) UV photolectron spectrum of Mo(t-BuS)$_4$ and its decomposition products. Each data points for the Mo(t-BuS)$_4$ spectrum was determined by collecting counts for 260 s. Photoelectron spectra for a) 2-methyl-2-propanethiol, b) 2-methyl-1-propene, c) di-t-butyl disulfide. Three peaks at (d) 9.61, (e) 10.26, and (f) 11.57eV originate from Xe ionizations. See text.

models of Mo(SH)$_4$ or Mo(SMe)$_4$ and Mo(NH$_2$)$_4$ with D_{2d} symmetry in calculations for Mo(t-BuS)$_4$ and Mo(NMe$_2$)$_4$ respectively, assuming that the effect of such distortion is negligible.

Results and Discussion

The UV photoelectron spectrum of Mo(t-BuS)$_4$ is shown in Fig. 2. There are at least four bands in Fig. 2. The first ionization band (IP=6.43 eV) is assigned an ionization of metal orbital because of its very low IP. The second band (IP=7.70 eV) is so sharp that it could be interpreted to correspond to the ionization of a nonbonding orbital. Over the very broad fourth band (IP=9—10 eV), there are two peaks of 9.03 eV and 9.06 eV which are in perfect agreement with the peaks in the photoelectron spectrum of 2-methyl-2-propanethiol. Therefore the peaks are most possibly assigned to the ionization of sulfur lone pair MOs of one of the decomposition products of Mo(t-BuS)$_4$. We presume that the peaks of 9.03 eV and 9.4 eV consist of the ionizations of 2-methyl-2-propanethiol and 2-methyl-1-propene (the spectra inserted in Fig. 2) respectively. Hence the spectral intensity due to the ionizations of those decomposition products should account for more than 70% of all the spectral intensity in the area of 9.0—9.8 eV, and in the area above 9.8 eV less than 35%. Furthermore there stand three peaks at 9.61 eV, 10.26 eV, and 11.57 eV, corresponding to the ionizations of xenon $^2P_{3/2}$ by HeIγ (23.74 eV) and HeIβ (23.09 eV), and $^2P_{1/2}$ by HeIβ, respectively.

TABLE 1. VERTICAL IONIZATION POTENTIALS FOR Mo(t-BuS)$_4$ AND CALCULATED ORBITAL ENERGIES FOR Mo(SH)$_4$ AND Mo(SMe)$_4$ (IN eV)

Observed IP Mo(t-BuS)$_4$	Orbital energies	
	Mo(SH)$_4$	Mo(SMe)$_4$
6.43	−3.26(13a$_1$)	−3.04(16a$_1$)
7.70	−4.33(2a$_2$)	−3.86(3a$_2$)
8.5	−4.77(13e)	−4.10(17e)
—	−5.45(12e)	−5.10(16e)

The vertical ionization potentials and computed orbital energies for Mo(SH)$_4$, and Mo(SMe)$_4$ are listed in Table 1. The molecular orbital energies are related to the vertical ionization potentials through Koopmans' theorem. The gross-orbital populations of filled and empty orbitals were calculated for Mo(SMe)$_4$ (Table 2). The calculation on Mo(SH)$_4$ gave similar results to those for Mo(SMe)$_4$ with respect to the bonding character between Mo and S. The first band (IP=6.43 eV) corresponds to the ionization of 16a$_1$ molecular orbital which consists mainly of metal 4d$_{z^2}$ orbital and partly of S3d and C2p orbitals. This orbital is of weakly bonding character between Mo4d-S3d and of antibonding between Mo4d-S3p$_z$ and Mo4d-S3s. Further this orbital has additional weak d-p bonding character for the ligand S–C bond.

The next two bands (IP=7.70 and 8.5 eV) are

TABLE 2. MOLECULAR ORBITAL COMPONENTS CALCULATED FOR Mo(SMe)$_4$ (IN %)

Level[a)]	Orbital energy/eV	Mo				S		
		4d$_{z^2}$	4d$_{x^2-y^2}$	4d$_{xy}$	4d$_{xz/yz}$	3d	3p	3s
5b$_1$	−1.14	—	54	—	—	5	40	0
16a$_1$[b)]	−3.04	56	—	—	—	13	8	5
3a$_2$	−3.86	—	—	—	—	0	93	0
17e	−4.10	—	—	—	0	0	96	0
16e	−5.10	—	—	—	17	1	66	6
15a$_1$	−5.29	9	—	—	—	1	69	2
4b$_1$	−5.51	—	37	—	—	4	55	0
14b$_2$	−5.57	—	—	35	—	2	56	2

a) Any contribution of other orbitals to the levels listed here is negligible except that 16a$_1$ contains 15% contribution of C2p, and 15a$_1$ contains 12% of Mo5s. b) This MO is the HOMO in Mo(SMe)$_4$.

assigned to the ionization of the molecular orbitals of 3a$_2$ and 17e levels, respectively. The 3a$_2$ level consists of only sulfur 3p lone pair MOs. The sharpness of the second band (IP=7.70 eV) supports this interpretation. The orbital of the 17e level consists of sulfur 3p lone pair MOs, too, and corresponds to the third band (IP=8.5 eV), which is slightly broader. The breadth of this band may be ascribed to be due to the Jahn-Teller effect. It is probable that the fourth band (IP>9 eV) contains the ionizations both of Mo(t-BuS)$_4$ and of decomposition products.

The complex, Mo(NMe$_2$)$_4$ or Mo(NEt$_2$)$_4$, is the only complex to our knowledge, which is analogous to Mo(t-BuS)$_4$ with respect to the molecular symmetry and the valence type of Mo, and for which UV photoelectron spectrum is known. Their spectra together with the Fenske-Hall type MO calculation on the model compound, Mo(NH$_2$)$_4$, have been reported by Chisholm *et al.*[12,13] In order to get an insight into the electronic structure of these complexes, the DV-Xα MO calculation was performed on the amidomolybdenum complex Mo(NH$_2$)$_4$ in addition to the thiolatomolybdenum complex. The result from the calculation on Mo(NH$_2$)$_4$ is consistent with that obtained by Chisholm *et al.*

The calculations on Mo(NH$_2$)$_4$ and Mo(SMe)$_4$ predict that the bond-overlap populations of Mo–N and Mo–S are 0.248 and 2.648, and that the net charge on Mo central atoms are +2.15 and +0.80, respectively. Therefore, it could be stated that the Mo–N bond is ionic in character but that the Mo–S bond is covalent if compared each other. The calculations also predict that the HOMO of the amidomolybdenum complex consists almost entirely of Mo4d$_{x^2-y^2}$ (88%), while that of the thiolatomolybdenum complex (16a$_1$) delocalizes slightly as shown in Table 2. The contents of this theoretical calculation appear to be inconsistent with the experimental fact that the half-width of the first band, corresponding to the ionization of the HOMO, in the spectrum of Mo(NMe$_2$)$_4$ is estimated to be about twice as large as that of Mo(t-BuS)$_4$ by comparing the published spectrum and the one in Fig. 2.

The difficulty to understand the contradiction has arisen in the same way on the studies of some metal-halide complexes.[14] For example, the photoionization of TlBr[15] gives a broad peak due to the ejection of the electron localized on Br *i.e.*, the "non-bonding" or "lone-pair electron," together with a sharp peak due to the ejection of the electron delocalized over the two atoms, *i.e.*, the "bonding electron" according to a molecular orbital model. The phenomenon was simply understood by taking account of the roles of localized and delocalized electrons in an ionic-bond. In the ionic-bond the electron on Br$^-$ acts as a bonding electron, so its ionization causes a broad peak. The present case of amidomolybdenum and thiolatomolybdenum complexes could be understood in quite the same manner. Thus the electron in HOMO of amidomolybdenum plays a role as an anti-bonding electron with respect to the ionic Mo–N bond more strongly than the corresponding electron in thiolatomolybdenum does as a bonding electron with respect to the covalent Mo–S bond. Therefore, the spectra exhibit the broader first band for the amidomolybdenum complex than for the thiolatomolybdenum complex.

The authors wish to thank Professor Hirohiko Adachi and Mr. Hirohide Nakamatsu for the computer program of the DV-Xα calculation. The numerical calculations were carried out using ACOS NEAC 900 at the Computation Center, Osaka University, and ACOS NEAC 700 at the Crystallographic Research Center Institute for Protein Research, Osaka University. This work was supported by Toray Science and Technology Grants 72-1302.

References

1) S. Otsuka, M. Kamata, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, **103**, 3011 (1981).

2) M. Kamata, T. Yoshida, and S. Otsuka, *J. Am. Chem. Soc.*, **103**, 3572 (1981).

3) S. O. Grim and L. J. Matienzo, *Inorg. Chem.*, **14**, 1014 (1975).

4) L. W. Yarbrough, II, and M. B. Hall, *Inorg. Chem.*, **17**, 2269 (1978).

5) B. Kim, H. Adachi, and S. Imoto, *J. Electron Spectrosc. Relat. Phenom.*, **11**, 349 (1977).

6) H. Adachi, *J. Electron Spectrosc. Relat. Phenom.*, **16**, 277 (1979); M. Sano, H. Adachi, and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **54**, 2636 (1981).

7) H. Ogata, H. Onizuka, Y. Nihei, and H. Kamada, *Bull. Chem. Soc. Jpn.*, **46**, 3036 (1973).

8) K. Kimura, S. Katsumata, T. Yamazaki, and H. Wakabayashi, *J. Electron Spectrosc. Relat. Phenom.*, **6**, 41 (1975).

9) G. Wagner and H. Bock, *Chem. Ber.*, **107**, 68 (1974).

10) H. Adachi, M. Tsukada, and C. Satoko, *J. Phys. Soc. Jpn.*, **45**, 875 (1978); C. Satoko, M. Tsukada, and H. Adachi, *ibid.*, **45**, 1333 (1978); H. Adachi, S. Shiokawa, M. Tsukada, C. Satoko, and S. Sugano, *ibid.*, **47**, 1528 (1979).

11) H. Nakamatsu, H. Adachi, and S. Ikeda, *J. Electron Spectrosc. Relat. Phenom.*, **24**, 149 (1981).

12) M. H. Chisholm, F. A. Cotton, and M. W. Extine, *Inorg. Chem.*, **17**, 1329 (1978).

13) M. H. Chisholm, A. H. Cowley, and M. Lattman, *J. Am. Chem. Soc.*, **102**, 46 (1980).

14) J. H. D. Eland, "Photoelectron Spectroscopy," Butterworths and Co., London (1974), pp. 126—128.

15) J. Berkowitz, *J. Chem. Phys.*, **56**, 2766 (1972).