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Absolute Stabilization Energies for Molybdenum 4d Electrons Based on the Reference Compound Tetrakis(dimethylamido)molybdenum(IV)

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The shift in the ionization potential of a molecular orbital that occurs when the molecule undergoes a substitutional modification is often difficult to interpret in terms of a change in the bonding character of the molecular orbital. One usually does not know how much of the shift is due to a change in potential (caused by changes in the charges of the atoms in the vicinity of the molecular orbital) and how much is due to a change in the relaxation energy associated with the ionization process. If the molecular orbital in question is largely located on one atom or a set of equivalent atoms, one can correct the ionization potential shift for the last two changes by subtracting eight-tenths of the corresponding shift in the core binding energy of the atom.[1-10] In other words, one can use core binding energies to calculate what the shift in ionization potential would be if there were no changes in potential and relaxation energy. Ideally, the molecular orbital of the reference molecule is a strictly nonbonding orbital, localized on one atom or one kind of atom. The calculated shifted ionization potential (for the second molecule) is then a localized orbital ionization potential (LOIP), or the value the ionization potential would have if the orbital were completely nonbonding.

Until now, the only molecules with strictly nonbonding valence electrons for which core binding energies and lone-pair ionization potentials were known were the hydrogen halides, H_2O, H_2S, H_2Se, planar NH_3, and planar PH_3. Thus it has been possible to apply the LOIP method on an *absolute* basis only in the case of compounds of F, Cl, Br, I, O, S, Se, N, and P. The LOIP method has been applied on a *relative* basis in the case of a few transition-metal MO's that are largely metal d in character.[2,6,8,10] For example, in $Mn(CO)_5H$, the e(Mn) orbital (which is composed mainly of the manganese d_{xz} and d_{yz} orbitals) can be used as a reference when studying the ionization potentials of the corresponding orbitals in the halides $Mn(CO)_5X$. In $Mn(CO)_5H$ there are no π-type interactions between the hydrogen atom and the manganese d orbitals; hence, the difference between the e(Mn) ionization potential of $Mn(CO)_5X$ and the e(Mn) LOIP of $Mn(CO)_5X$ (calculated with $Mn(CO)_5H$ as the reference) can be taken as a measure of the interaction of the halogen $p\pi$ orbitals with the e(Mn) orbital. However, it has not been possible to determine the absolute stabilization or destabilization of a metal d orbital in a compound relative to a strictly nonbonding metal d orbital because the required data for a compound containing a strictly nonbonding d orbital have not been available.

However, we now have the required data for one compound, $Mo[N(CH_3)_2]_4$, which possesses an essentially nonbonding d electron pair. This molecule adopts the D_{2d} geometry of an elongated tetrahedron, in which the two molybdenum 4d electrons are expected to occupy a $b_1(x^2 - y^2)$ orbital.[11] The molecule possesses no other valence-shell orbital of b_1 symmetry, and so this pair of electrons should be strictly nonbonding. The ultraviolet photoelectron spectrum of $Mo[N(CH_3)_2]_4$ is consistent with this interpretation; a peak at 5.30 eV corresponding to the molybdenum 4d electrons is very sharp, as expected for a nonbonding orbital.[12]

Table I. Core Binding Energies and Mo 4d Ionization Potential Data (eV) for Molybdenum Compounds

compd	E_B (Mo $3d_{5/2}$)	IP (Mo 4d)	LOIP (Mo 4d)	IP − LOIP
$Mo[N(CH_3)_2]_4$	234.04[a]	5.30[b]	(5.30)	(0.0)
$Mo(CO)_6$	234.56[c,d]	8.50[e]	5.72	2.78
$Mo(CO)_5P(CH_3)_3$	233.78[c,f]	7.60[d]	5.09	2.51
		7.87[d]	5.09	2.78
$Mo(CO)_5P[N(CH_3)_2]_3$	233.76[c]	7.65[g]	5.07	2.58
		7.87[g]	5.07	2.80
$Mo(CO)_5P(OC_2H_5)_3$	234.08[c]	7.87[g]	5.33	2.54
		8.06[g]	5.33	2.73
$Mo(CO)_5P(OCH_3)_3$	234.03[c]	7.97[g]	5.30	2.67
		8.17[g]	5.30	2.87
$Mo(CO)_5PCl_3$	234.37[c]	8.23[h]	5.56	2.67
		8.43[h]	5.56	2.87
$Mo(CO)_5PF_3$	234.56[c]	8.42[i]	5.72	2.70
		8.62[i]	5.72	2.90
cis-$Mo(CO)_4[P(CH_3)_3]_2$	233.09[f]	6.84[d]	4.54	2.30
		7.14[d]	4.54	2.60
trans-$Mo(CO)_4[P(CH_3)_3]_2$	233.03[f]	6.82[d]	4.49	2.33
		7.31[d]	4.49	2.82
fac-$Mo(CO)_3[P(CH_3)_3]_3$	232.55[f]	6.48[d]	4.11	2.37
$Mo_2(O_2CH)_4$	235.3[j]	~7.7[k,l]	6.3	~1.4
$Mo_2(O_2CCH_3)_4$	234.7[j]	6.98[m]	5.8	1.2
$Mo_2(mhp)_4$[n]	233.8[j]	~5.8[o]	5.1	~0.7

[a] From this work. [b] Reference 12. [c] Jolly, W. L.; Bomben, K. D.; Eyermann, C. J. *At. Data Nucl. Data Tables* **1984**, *31*, 433. [d] Bursten, B. E.; Darensbourg, D. J.; Kellogg, G. E.; Lichtenberger, D. L. *Inorg. Chem.* **1984**, *23*, 4361. [e] Higginson, B. R.; Lloyd, D. R.; Burroughs, P.; Gibson, D. M.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1659. [f] Reference 10. [g] Calculated from the e–b_2 splittings and rough band positions reported in ref 13. The absolute values are probably ±0.1 eV. [h] Calculated from an estimated e–b_2 splitting and the band position reported in: Daamen, H.; Boxhoorn, G.; Oskam, A. *Inorg. Chim. Acta* **1978**, *28*, 263. [i] Calculated from the e–b_2 splitting of ref 13 and the band position of Daamen et al. [j] Atha, P. M.; Berry, M.; Garner, C. D.; Hillier, I. H.; Macdowell, A. A. *J. Chem. Soc., Chem. Commun.* **1981**, 1027. [k] Green, J. C.; Hayes, A. J. *J. Chem. Phys. Lett.* **1975**, *31*, 306. [l] Cotton, F. A.; Norman, J. G.; Stults, B. R.; Webb, T. R. *J. Coord. Chem.* **1976**, *5*, 217. [m] Lichtenberger, D. L.; Blevins, C. H. *J. Am. Chem. Soc.* **1984**, *106*, 1636. [n] mhp is the anion of 2-hydroxy-6-methylpyridine. [o] F. A. Cotton, A. H. Cowley, and M. Lattman quoted in: Cowley, A. H. *Prog. Inorg. Chem.* **1979**, *26*, 45.

In this study, we determined the Mo $3d_{5/2}$, N 1s, and C 1s binding energies of $Mo[N(CH_3)_2]_4$ in the vapor phase. The Mo $3d_{5/2}$ binding energy can be used in conjunction with the ionization potential of other molybdenum compounds to quantify the bonding characters of molecular orbitals derived from the molybdenum

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4d orbitals in these compounds. In Table I we have summarized the relevant data for a number of molybdenum compounds. Consider, for example, molybdenum hexacarbonyl. Here the ionization potential of the t_{2g} electrons (8.50 eV) is 2.78 eV higher than the LOIP (the value that the ionization potential would have if the t_{2g} electrons were strictly nonbonding, i.e. 5.72 eV). Thus for the first time we have an experimental value for the stabilization of the t_{2g} orbitals in $Mo(CO)_6$ caused by back-bonding to the carbonyl groups.

Table I includes two ionization potentials for each of six compounds of the type $Mo(CO)_5PX_3$. In each case the lower ionization potential corresponds to the e(Mo) orbital, which has the same symmetry as the π orbitals of the PX_3 group, and the higher ionization potential corresponds to the b_2(Mo) orbital, which is orthogonal to the π orbitals of the PX_3 group. All the b_2 stabilization energies fall in the range 2.78–2.90 eV, essentially equal to the stabilization energy of $Mo(CO)_6$. All the e stabilization energies fall in the range 2.51–2.70 eV, slightly lower than the stabilization energy of $Mo(CO)_6$. It is not surprising that all the ionization potentials of the b_2 orbitals, which can interact with four CO groups, are greater than the ionization potentials of the e orbitals, each of which can interact with three CO groups and the PX_3 group. This observation, which has been previously discussed by Yarbrough and Hall,[13] is consistent with the assumption that all of the PX_3 groups are poorer π acceptors than CO. The fact, revealed by the present data, that all the stabilization energies of the b_2 orbitals are very similar in magnitude to the stabilization energy of the t_2 orbitals of $Mo(CO)_6$ is also not surprising. This fact merely serves as another confirmation of the validity of the general LOIP method. However, we were surprised by the fact that, in all the $Mo(CO)_5PX_3$ compounds, the *percentage* reduction in the stabilization energy as one goes from the b_2 to the e orbital (i.e., on replacement of one of four CO groups by a PX_3 group) is only about 10% or less. The data clearly show that, when one of the four CO groups that interact with a $d\pi$ orbital is replaced by a PX_3 group, the three remaining CO groups *almost completely* take up the slack in back-bonding. Although this qualitative behavior has long been assumed in rationalizations of the trans effect, it has not been recognized that CO ligands are so resilient that they can almost completely compensate for the reduction in ligand π acceptance when a CO ligand is replaced by a relatively poor π-acceptor ligand such as $P(CH_3)_3$.

Table I also contains data for *cis*- and *trans*-$Mo(CO)_4[P(CH_3)_3]_2$ and *fac*-$Mo(CO)_3[P(CH_3)_3]_3$. As expected, the stabilization energy of the d_{xy} orbital of *trans*-$Mo(CO)_4[P(CH_3)_3]_2$, 2.82 eV, is essentially the same as the t_{2g} stabilization energy of $Mo(CO)_6$. The stabilization energies of all the other d orbitals (which could conceivably engage in π interactions with the $P(CH_3)_3$ ligands) are 2.30, 2.60, and 2.33 for *cis*- and *trans*-$Mo(CO)_4[P(CH_3)_3]_2$ and 2.37 eV for *fac*-$Mo(CO)_3[P(CH_3)_3]_3$. These values are significantly lower than the t_{2g} stabilization energy of $Mo(CO)_6$. Thus the data are consistent with a steady decrease in the overall back-bonding of the molybdenum $d\pi$ orbitals as CO ligands are stepwise replaced with $P(CH_3)_3$ ligands.

Next consider the dimolybdenum tetracarboxylates $Mo_2(O_2CH)_4$, $Mo_2(O_2CCH_3)_4$, and $Mo_2(mhp)_4$. The Mo 4d ionization potentials listed for these molecules correspond to the Mo–Mo δ-bonding orbitals. The stabilization energies, as measured by the IP – LOIP values, are all around 1 eV, indicating that the δ contributions to these Mo–Mo quadruple bonds are quite substantial.

Experimental Section

Tetrakis(dimethylamido)molybdenum(IV) was prepared from $LiN(CH_3)_2$ and $MoCl_5$.[14] The product was purified by two sublimations (10^{-3} torr) at room temperature onto a −20 °C cold finger. The infrared and mass spectra agreed with those in the literature.[14] Vapor-phase X-ray photoelectron spectra were obtained with a GCA/McPherson ESCA-36 spectrometer using a Mg anode. The vapor from a sample held at 10 °C diffused directly into the spectrometer gas cell through large diameter (1.5-cm) tubing. The spectra were calibrated against the N 1s line of admixed N_2 gas, with a correction for spectrometer nonlinearity determined by Ne 1s, N_2 1s, and Ne 2s calibration lines at 870.37, 409.93, and 48.47 eV, respectively. The binding energies and full width at half-maximum (fwhm) values (eV) were 234.04 (3) and 1.11 (12) for Mo $3d_{5/2}$, 403.14 (4) and 1.08 (14) for N 1s, and 290.66 (3) and 1.16 (12) for C 1s. (The 2σ values of least-squares fits of the data are indicated parenthetically.)

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Registry No. $Mo[N(CH_3)_2]_4$, 100207-68-9; $Mo(CO)_6$, 13939-06-5; $Mo(CO)_5P(CH_3)_3$, 16917-96-7; $Mo(CO)_5P[N(CH_3)_2]_3$, 14971-43-8; $Mo(CO)_5P(OC_2H_5)_3$, 15603-75-5; $Mo(CO)_5P(OCH_3)_3$, 15631-20-6; $Mo(CO)_5PCl_3$, 19212-18-1; $Mo(CO)_5PF_3$, 15322-05-1; *cis*-$Mo(CO)_4[P(CH_3)_3]_2$, 16027-45-5; *trans*-$Mo(CO)_4[P(CH_3)_3]_2$, 30513-03-2; *fac*-$Mo(CO)_3[P(CH_3)_3]_3$, 19195-94-9; $Mo_2(O_2CH)_4$, 51329-49-8; $Mo_2(O_2CCH_3)_4$, 14221-06-8; $Mo_2(mhp)_4$, 67634-80-4.

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The ^{18}O Isotope Shift in ^{15}N NMR Spectroscopy. 2. Synthesis of $^{15}N,^{18}O$-Labeled Hydroxylamine Hydrochloride

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Substitution of oxygen-18 for oxygen-16 results in detectable upfield shifts on the NMR signals of many nuclei including ^{13}C, ^{31}P, and ^{15}N, when they are directly bonded to oxygen.[1-3] These upfield shifts provide a convenient and direct method of following enzymatic and nonenzymatic oxygen-exchange reactions occurring at carbon,[4,5] phosphorus,[2,6] and nitrogen.[3] The ^{18}O-induced isotope shift in ^{15}N NMR has been utilized in studies of the oxidation of ammonium ion to nitrite by a *Nitrosomonas* species[7] and nitrite to nitrate by *Nitrobacter agilis*,[8] but otherwise the technique has not yet found wide applications. This is due in part to the lack of a systematic study of the characteristics of the ^{18}O isotope shift in ^{15}N NMR spectra of various compounds. Consequently, we have undertaken the synthesis of various types of compounds containing N–O groupings with both ^{15}N and ^{18}O isotopic enrichment, as well as examination of their ^{15}N NMR spectral properties.

Studies on the synthesis of $^{15}N,^{18}O$ dual-labeled compounds are limited to sodium and silver nitrites, sodium nitrate, some oxides of nitrogen, and alkyl nitrites and nitrates.[9-11] Experiments

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