

THE NATURE AND SPECTROSCOPIC CHARACTER OF THE METAL-OXYGEN BONDING OF SOME HEAVY METALS. PART II*
THE LENGTH AND BOND ORDER OF THE METAL-OXYGEN BONDING IN OXY-COMPOUNDS OF RHENIUM, TECHNETIUM OSMIUM AND RUTHENIUM ON THE BASIS OF INFRA-RED SPECTROSCOPY

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In the present work some infra-red spectra of rhenium, technetium, osmium and ruthenium oxy-complexes are used for calculating the metal-oxygen bond order and for estimating its length. For this purpose, empirical equations developed by Siebert and Badger are used. On the basis of the results obtained the contribution of $d_{\pi}-p_{\pi}$ interaction to the metal-oxygen bonding is discussed.

1. Bond order calculation

The expression "bond order" is employed to describe the multiplicity of the bonding between two atoms. It is utilized in various ways; its strict meaning should be, therefore, derived from a notional association. Should this term be used in connection with the molecular orbitals of molecules, then the bond order determines the number of electron pairs in resultant bonding action. When the term "bond order" is used in connection with the directional valence, its meaning is slightly different, as it is employed to provide information on the number of σ and π bonds which combine to yield a link between two atoms. The overall bond order is a total number of bonds between the atoms and the mobile bond order is the number of π bonds between them. There is a rather close analogy between the terms so defined, which gives in effect close numerical values in both cases.

Introduction of the term "bond order" into the LCAO-MO theory was suggested by

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Coulson [1]. His definition for poly-atomic molecules containing one AO per atom, pertaining to the linear combinations of the expression

$$\Phi_i = \sum_r d_{ir} \psi_i$$

is expressed by the relationship

$$p_i(r, s) = N(i) \sum_{s>r} d_{ir} d_{is}$$

$$p = \sum_i p_i(r, s) \quad (N - \text{number of electrons})$$

and derived with the overlap integrals S_{rs} being neglected.

Modifications of this definition, as suggested by Mulliken [2, 3], Coulson [4] and Pullman [5], include the overlap integrals. Respective bond order equations $p(r, s)$ assume the following form:

$$d_{ir} = v_i C_r \quad v_i^2 = \frac{1}{\sum_r C_r^2}$$

$$p_i(r, s) = N(i) d_{ir} d_{is} \quad \text{or} \quad p_i(r_k, s_l) = N(i) (1 + S_{r_k s_l}) d_{ir_k} d_{is_l}$$

$$p(r, s) = \sum_i p_i(r, s) \quad p_i(k, l) = \sum_{i>k} p_i(r_k, s_l)$$

$$p(k, l) = \sum_i p_i(k, l)$$

where c_r , c_s , d_{ir} and d_{is} correspond to the coefficients in the linear combination of atomic orbitals.

Calculation of the bond order by analyzing the electronic configuration is, therefore, time-consuming, and in each case it is necessary to know the overlap integral. The value obtained on the basis of any one of the definitions presented is almost, but not quite, equal to values obtained with the use of the other definitions, and even this is subject to controversy.

Recently, several papers have been published in which vibrational spectroscopy is employed for estimating the bond order in compounds and also for estimating the bond length. An equation which is most frequently employed for calculating the bond order is the so-called "Siebert product principle" [6] which utilizes the concept of an "X-Y covalent bonding force constant", defined as:

$$f_{XY} = 7.2 \frac{Z_X Z_Y}{n_X^3 n_Y^3} [\text{Md}/\text{\AA}]$$

where Z_X and Z_Y are the atomic numbers of the elements X and Y, respectively, and n_X and n_Y are the principal quantum numbers of valency electrons for X and Y atoms, respectively. Using the above equation, Siebert [6] derived empirical equations for the bond order, in which the experimental values of a "vibrational force constant" f_r determined

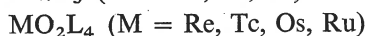
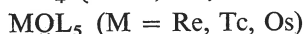
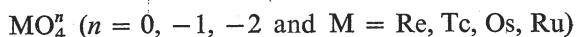
from the IR or Ra spectra are introduced. These equations are as follows:

$$N = 0.69 \frac{f_r}{f_{XY}} + 0.37 \quad \text{if} \quad \frac{f_r}{f_{XY}} > 1.5$$

$$N = \frac{f_r}{f_{XY}} \quad \text{if} \quad 0 < \frac{f_r}{f_{XY}} < 1.5$$

where N is the bond order.

These equations were utilized in the present work to calculate the metal-oxygen bond order for a number of mononuclear oxy-compounds of rhenium, technetium, osmium and ruthenium of general formulae:



and for binuclear complexes containing a bridging $\text{M}-\text{O}-\text{M}$ group ($M = \text{Re, Os, Ru}$). The infra-red spectra of the above compounds, together with their assignments, were presented in our earlier paper [7], in which the spectroscopic characteristics of oxy-compounds were given and each oxygen system was assigned a definite vibrational absorption region. On the basis of the derived approximate secular equations the metal-oxygen force constants for each case were calculated. These are used in the present work in calculations of the metal-oxygen bond order and determinations of the contribution of $d_\pi-p_\pi$ interactions to this bonding.

The metal-oxygen bond orders calculated from the Siebert equation for each type of oxy-compounds are shown in Tables I-VI. The "covalent force constants" f_{MO} for rhe-

TABLE I
Metal-oxygen bond length and bond order in MO_3L_3 type compounds

Complex	Stretching force constant f_r [Md/Å]	Bond order	Bond length [Å]
$\text{Cs}_2[\text{ReO}_3\text{Cl}_3]$	6.96	2.22	1.76
$\text{Cs}[\text{OsO}_3\text{F}_3]$	7.47	2.40	1.74

TABLE II
Metal-oxygen bond length and bond order in MO_4^n type compounds

Compound	f_r [Md/Å]	f_r/f_{MO}	Bond order	Bond length
ReO_4^-	7.52	3.01	2.45	1.74
OsO_4	8.05	3.18	2.56	1.73
RuO_4	6.73	2.66	2.21	1.71
RuO_4^-	5.82	2.30	1.96	1.74
RuO_4^-	5.56	2.20	1.89	1.75
TcO_4^-	6.74	2.72	2.25	1.75

TABLE III

Metal-oxygen bond length and bond order in MOL_5 type complexes

Complex	f_r [Md/Å]	f_r/f_{MO}	Bond order	Bond length [Å]
$K_2[ReOCl_5]$	8.36	3.34	2.68	1.72
$Cs_2[ReOCl_5]$	7.91	3.16	2.55	1.73
$Cs_2[ReOCl_4 F]$	8.21	3.28	2.63	1.72
$[ReO(OH)en_2]Cl_2$	8.35	3.34	2.68	1.72
$[ReO(OH)py_4]Cl_2$	8.08	3.23	2.60	1.73
$ReOCl_3en$	8.16	3.26	2.62	1.73
$ReOCl_3py_2$	8.18	3.27	2.63	1.73
$OsOF_5$	8.01	3.17	2.55	1.73
$(NH_4)_2[TcOCl_5]$	7.92-7.84	3.19-3.16	2.57-2.55	1.72
$K_2[TcOCl_5]$	7.98-7.88	3.22-3.18	2.59-2.56	1.72
$Cs_2[TcOCl_5]$	7.41	2.96	2.14	1.73

TABLE IV

Metal-oxygen bond length and bond order in MO_2L_4 type complexes

Complex	Stretching force constant	Bond order	Bond length [Å]
$[ReO_2en_2]Cl$	6.43	2.14	1.77
$[ReO_2py_4]Cl$	6.45	2.15	1.77
$K_3[ReO_2(CN)_4] \cdot aq$	6.06	2.04	1.78
$[ReO_2(NH_3)_4]Cl$	6.45	2.15	1.77
$K_2[OsO_2Cl_4]$	6.64	2.18	1.76
$(NH_4)_2[OsO_2Cl_4]$	6.67	2.19	1.76
$Cs_2[OsO_2Cl_4]$	6.63	2.18	1.76
$K_2[OsO_2Br_4]$	6.68	2.19	1.76
$(NH_4)_2[OsO_2Br_4]$	6.65	2.18	1.76
$K_2[OsO_2(OH)_4]$	6.09	2.02	1.78
$K_2[OsO_2(NO_2)_4]$	6.67	2.19	1.76
$K_2[OsO_2(C_2O_4)_2]$	6.69	2.20	1.76
$Cs_2[OsO_2(C_2O_4)_2]$	6.66	2.19	1.76
$K_2[OsO_2(CN)_4]$	6.51	2.14	1.77
$Cs_2[OsO_2(CN)_4]$	6.55	2.15	1.77
$Ag_2[OsO_2(CN)_4]$	6.52	2.14	1.77
$K_4[Os_2O_6(NO_2)_4]$	6.59	2.16	1.77
$K_4[Os_2O_6(C_2O_4)_2]$	6.59	2.16	1.77
$[OsO_2(NH_3)_4]Cl_2$	6.33	2.09	1.77
$[OsO_2(NH_3)_4](OH)_2$	6.35	2.10	1.77
$[OsO_2(NH_3)_4]SO_4$	6.41	2.11	1.77
$Cs_2[RuO_2Cl_4]$	5.56	1.89	1.75
$Rb_2[RuO_2Cl_4]$	5.54	1.88	1.75
$[Cs_2RuO_2Br_4]$	5.60	1.91	1.75
$[As(phen)_4]_2[RuO_2Br_4]$	5.54	1.88	1.75
$[As(phen)_4]_2[RuO_2(SO_4)_2]$	5.50	1.86	1.75
$[Ru_2O_6(NH_3)_4]$	5.53	1.87	1.75
$[TcO_2en_2]Cl$	6.23	2.10	1.77

TABLE V

Metal-oxygen bond length and bond order in the dinuclear M_2OL_{10} type complexes

Complex	Stretching force constant f_r [Md/Å]	Bond order	Bond length
$K_4[Re_2OCl_{10}]$	3.84	1.53	1.88
$Cs_4[Re_2OCl_{10}]$	3.87	1.55	1.88
$[Re_2O_3en_2Cl_4]$	3.40	1.36	1.90
$[Re_2O_3py_4Cl_4]$	3.30	1.32	1.91
$K_6[Re_2O_3(CN)_8]$	3.47	1.39	1.90
$(NH_4)_4[Os_2OCl_{10}]$	3.97	1.57	1.87
$Y_4^*[Os_2OCl_{10}]$	3.94	1.56	1.87
$Cs_4[Os_2OBr_{10}]$	3.96	1.57	1.87
$Y_4[Os_2OBr_{10}]$	3.97	1.57	1.87
$Cs_4[Os_2OI_{10}]$	3.92	1.55	1.87
$Y_4[Os_2OI_{10}]$	3.95	1.56	1.87
$Cs_4[Os_2OCl_6Br_4]$	3.98	1.57	1.87
$Y_4[Os_2OCl_6Br_4]$	3.94	1.56	1.87
$Cs_4[Os_2OCl_8I_2]$	4.15	1.64	1.86
$K_4[Ru_2OCl_{10}]$	3.57	1.41	1.85
$Y_4[Ru_2OCl_{10}]$	3.55	1.40	1.85
$K_4[Ru_2OBr_{10}]$	3.46	1.37	1.86
$Y_4[Ru_2OBr_{10}]$	3.47	1.37	1.86
$Y_4[Ru_2OBr_2Cl_8]$	3.37	1.33	1.86

* $Y = [As(phen)_4]$.

TABLE VI

Metal-oxygen bond length and bond order in hydroxy-complexes

Complex	f_r [Md/Å]	Bond order	Bond length
$[Re(OH)_2en_2]Cl_3$	2.99	1.19	1.94
$[Re(OH)_2en_2]F_3$	2.82	1.12	1.95
$[ReO(OH)en_2]Cl_2$	2.93	1.17	1.945
$[Ru(OH)(NH_3)_4(NO)]Cl_2$	2.82	1.11	1.91
$[Ru(OH)(NH_3)_4(NO)]Br_2$	2.89	1.14	1.92
$K_2[Ru(OH)(NO_2)_4(NO)]$	2.92	1.15	1.90

nium, technetium, osmium and ruthenium are 2.50, 2.48, 2.53 and 2.53, respectively. The numerical values of bond order, which are a measure of the total bonding effect ($\sigma + \pi$), indicate a considerable contribution of π electrons to the metal-oxygen bonding. This contribution, as expressed, decreases in the series:

$$N_{MO} > N_{MO_3} > N_{MO_2} > N_{M-O-M} > N_{M-OH}$$

Vibrational spectroscopy thus confirms the conclusions obtained from studies of the π electron distribution in molecular orbitals of metal-oxygen bondings in the oxy-complexes under investigation.

Considering the orbital transformation scheme for C_{4v} symmetry in MOL_5 type complexes, the σ -bonding of the oxy-group (symmetry A_1) is found to be formed by means of the metal $s + d_{z^2}$ orbitals and oxygen sp_σ orbitals, the other σ -bonds are formed from the $s - d_{z^2}$, p_x , p_y , p_z and $d_{x^2-y^2}$ orbitals. The $d_{xy}B_2$ orbital is non-bonding. Finally, the two metal d_{xz} and d_{yz} orbitals (symmetry E) may interact with the oxygen p_x and p_y orbitals, whereby two additional $p_\pi - d_\pi$ bondings between the oxygen and metal are formed. Because of certain π -bonding properties of ligands, the contribution of this bonding to the overall metal-oxygen bonding causes that the latter has a bond order of 2.5 to 2.8 (as calculated by means of the overlap integrals) [8], which is consistent with the results of our present calculations.

Strong σ -bondings are formed in the MO_2L_4 complex of D_{4h} symmetry by means of the metal $s \pm d_{z^2}$, $d_{x^2-y^2}$, p_x , p_y and p_z orbitals and suitable linear combinations of the ligand orbitals. On the other hand, two strong $d_\pi - p_\pi$ bonds exist between the metal atom and two trans oxygen atoms (that is, one π -bonding per each metal-oxygen σ -bonding) resulting from interactions between the metal d_{xz} , d_{yz} orbitals and the oxygen p_x , p_y orbitals (symmetry E_g). Hence, the metal-oxygen bonding in trans-di-oxy groups is weaker than in mono-oxy groups; the order of this bond, as shown in the present discussion, is close to 2. This was also confirmed by our results obtained by the vibrational-spectroscopic methods.

Without any detailed theoretical discussion on the MO_3L_3 systems one may state that the bond order in this case should be intermediate between those occurring in the mono- and di-oxy compounds, as confirmed by experiment (Table I and VIII).

It is interesting to note that the metal-oxygen bond order in binuclear M_2OL_{10} type complexes is 1.3–1.7 (Table V). The lower 1.3 limit of the bond order is observed in compounds which contain a linear $O - M - O - M - O$ group. In such compounds the influence of outer oxygens *via* "electron withdrawing effect" results in a weakening of the bridging oxygen bonding. In other cases the bond order is approximately 1.5, that is 0.5 π -bonding per σ -bonding and, hence, the bridged group are fairly stable.

The metal-oxygen bond order in hydroxy-compounds range from 1.11 to 1.19, and this also suggests a small π -bonding contribution to the overall bonding effect. This magnitude is the most probable one since a pure σ -bonding should occur in the $M(H_2O)_xL_{6-x}$ aquo-complexes, in which the metal-oxygen bonding is effected through the oxygen from the water molecule.

2. Calculation of the metal-oxygen bond length

Vibrational spectroscopy also makes possible the estimation of the lengths of bonds for which the force constants have been determined from the IR or Ra spectra. The Badger equation [9] is the most frequently used for this purpose,

$$R_{XY} = \alpha f_r^{-1/3} + \beta$$

although the equation of Clark [10]

$$R_{XY}^2 = C \left(\frac{\mu}{nf_r} \right)^{1/3}$$

and that of Allen [11]

$$R_{XY}^2 = C' f_r^{-1/3}$$

have also been studied.

In these equations α , β , μ and C denote the constants characteristic of the bond-forming elements. These parameters are usually determined by experiment.

In the present work the Badger equation was utilized and its correctness was repeatedly checked by comparing the results obtained with the use of X-ray structural data. The α and β coefficients of this equation may be determined by a method suggested by Jones [12]. It assumes that if f_r is expressed in [Md/Å] and R in [Å], then $\alpha \approx 1.08$ for all pairs of elements as long as the atomic number of one element is higher than 18 (this is consistent with Badger's observations [9]). Under this assumption, β is determined for the R_{XY} value obtained by the X-ray method and its corresponding force constant.

Table VII shows the structural data which were utilized in calculations of the α and β coefficients of metal-oxygen bondings in the oxy-compounds discussed in the present paper.

TABLE VII

Structural data used in calculations of α and β coefficients

Bond	Compound	Bond length [Å]	Ref.	Force constant f [Md/Å]	Coefficient		
					α	β	$\bar{\beta}$
rhenium-oxygen	K ₂ [ReOCl ₅]	1.66 ± 0.03	[13]	8.36	1.08	1.13	1.19
	KReO ₄	1.77	[14]	7.52		1.22	
	K ₃ [ReO ₂ (CN) ₄]	1.87	[15]	6.06		1.23	
	K ₄ [Re ₂ OCl ₁₀]	1.86	[16]	3.84		1.17	
technetium-oxygen	KTcO ₄	1.75	[17]	6.74	1.08	1.18	1.18
osmium-oxygen	OsOF ₅	1.74 ± 0.03	[18]	8.01	1.08	1.20	1.19
	K ₂ [OsO ₂ Cl ₄]	1.75 ± 0.02	[19]	6.65		1.18	
	K ₂ [OsO ₂ (OH) ₄]	1.77	[20]	6.09		1.18	
ruthenium-oxygen	RuO ₄	1.705	[21]	6.73	1.08	1.13	1.14
	KRuO ₄	1.79	[22]	5.82		1.19	
	K ₄ [Ru ₂ OCl ₁₀]	1.80	[23]	3.57		1.09	

Empirical Badger equations giving the relationship between the bond length and force constant determined by experiment assume the following linear forms for each particular metal:

$$R_{ReO} = 1.08 f_r^{-1/3} + 1.19$$

$$R_{TcO} = 1.08 f_r^{-1/3} + 1.18$$

$$R_{OsO} = 1.08 f_r^{-1/3} + 1.19$$

$$R_{RuO} = 1.08 f_r^{-1/3} + 1.14$$

TABLE VIII

Correlation between vibration frequency, force constant, bond length and bond order of the metal-oxygen bonding (M = Re, Tc, Os, Ru)

Type of complex	Vibration frequency [cm ⁻¹]	Bond order	Bond length [Å]	Stretching force constant [Md/Å]
MOL ₅	950-995	2.41-2.68	1.72-1.73	7.41-8.36
MO ₄	860-940	1.89-2.56	1.71-1.75	5.56-8.05
MO ₃ L ₃	890-952	2.22-2.40	1.74-1.76	6.96-7.47
MO ₂ L ₄	775-905	1.86-2.19	1.75-1.78	5.50-6.68
M-O-M	700-880	1.33-1.64	1.85-1.91	3.37-4.15
	200-250			
M-OH	448-580	1.11-1.19	1.90-1.95	2.82-2.99

The metal-oxygen distances calculated from these equations for oxy-bonds in the complexes under investigation are shown in Tables I to VI.

A full correlation of the results obtained, that is force constants, bond orders, bond lengths and vibration frequencies, are given in Table VIII.

X-ray analysis of the oxy-compounds dealt with in this work, performed at the present in our Laboratory, should yield more accurate data of the structural parameters.

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