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William L. Jolly, Steven C. Avanzino, and Richard R. Rietz

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Contribution from the Department of Chemistry, University of California, and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720.

The Use of Oxygen 1s Binding Energies and Multiplicity-Weighted C-O Stretching Frequencies to Measure Back-Bonding in Transition Metal Carbonyl Complexes

William L. Jolly*, Steven C. Avanzino and Richard R. Rietz
Back-bonding in a transition metal carbonyl involves a decrease in the C-O bond order of the carbon monoxide ligand:

\[
\text{M} - \text{C} \equiv \text{O}^+ \quad \leftrightarrow \quad \text{M} \equiv \text{C} = \text{O}
\]

Because a decrease of bond order corresponds to a decrease of bond strength, the C-O stretching frequencies (or the derived force constants) of transition metal carbonyls have commonly been used to measure the degree of back-bonding. Unfortunately there are very few other physical properties which can be used to measure back-bonding and which are correlated with the stretching frequencies or force constants. Carbon-13 nmr chemical shifts have been shown to be related to the degree of back-bonding in carbonyls, but good correlations with C-O stretching frequencies have been obtained only for restricted sets of compounds, in which the structures are very similar.

Because back-bonding in a carbonyl involves a shift of negative charge from the metal atom to the oxygen atoms of the CO ligands, we anticipated that O 1s binding energies would be closely correlated with back-bonding. During the last few years we have measured these binding energies for a wide variety of transition metal carbonyl complexes in which the CO ligands are terminally bound. The data are given in Table I. One would expect a correlation of the O 1s binding energies with the corresponding C-O stretching force constants. Unfortunately the force constants have not been calculated for all the molecules in Table I and could not be readily calculated without making some rather poor approximations. As an alternative to the use of force constants, we have used the multiplicity-weighted averages of the C-O stretching
Table I.

Correlation of Oxygen 1s Binding Energies of Carbonyl Complexes with Back-Bonding

<table>
<thead>
<tr>
<th>Carbonyl Cpd.</th>
<th>(E_B(O,1s), \text{eV})</th>
<th>(v_{CO}, \text{cm}^{-1})</th>
<th>((n_V + n_{CO}))</th>
<th>(v_{CO})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_6\text{H}_6\text{Cr(CO)}_3)</td>
<td>538.23</td>
<td>1938</td>
<td>10</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>(\text{C}_7\text{H}_7\text{V(CO)}_3)</td>
<td>538.6</td>
<td>1935</td>
<td>10</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>(\text{C}_5\text{H}_5\text{V(CO)}_4)</td>
<td>538.7</td>
<td>1963</td>
<td>10</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>(\text{C}_5\text{H}_5\text{(CH}_3\text{)Mo(CO)}_3)</td>
<td>538.8</td>
<td>1971</td>
<td>10</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>(\text{C}_5\text{H}_5\text{Mn(CO)}_9)</td>
<td>538.85</td>
<td>1974</td>
<td>11</td>
<td>10</td>
<td></td>
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<tr>
<td>(\text{Mn}_2\text{(CO)}_10)</td>
<td>538.89</td>
<td>2017</td>
<td>12</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>(\text{C}_7\text{H}_8\text{Fe(CO)}_3)</td>
<td>539.09</td>
<td>2004</td>
<td>12</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_3\text{(OCH}_3\text{)CCr(CO)}_5)</td>
<td>539.1</td>
<td>1984</td>
<td>12</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>(\text{C}_4\text{H}_6\text{Fe(CO)}_3)</td>
<td>539.29</td>
<td>2005</td>
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<td>13</td>
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<tr>
<td>(\text{W(CO)}_6)</td>
<td>539.52</td>
<td>2017</td>
<td>12</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>(\text{Mo(CO)}_6)</td>
<td>539.61</td>
<td>2021</td>
<td>12</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_3\text{Re(CO)}_5)</td>
<td>539.64</td>
<td>2033</td>
<td>12</td>
<td>14</td>
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<tr>
<td>(\text{Cr(CO)}_6)</td>
<td>539.66</td>
<td>2018</td>
<td>12</td>
<td>10</td>
<td></td>
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<tr>
<td>(\text{HMn(CO)}_5)</td>
<td>539.84</td>
<td>2039</td>
<td>12</td>
<td>15</td>
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<tr>
<td>(\text{CH}_3\text{Mn(CO)}_5)</td>
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<tr>
<td>(\text{V(CO)}_6)</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>(\text{CH}_3\text{COMn(CO)}_5)</td>
<td>539.92</td>
<td>2038</td>
<td>12.5</td>
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<tr>
<td>(\text{Fe(CO)}_5)</td>
<td>540.00</td>
<td>2035</td>
<td>13</td>
<td>10</td>
<td></td>
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<td>(\text{Ni(CO)}_4)</td>
<td>540.11</td>
<td>2066</td>
<td>14</td>
<td>10</td>
<td></td>
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<tr>
<td>(\text{Cl}_3\text{SiMn(CO)}_5)</td>
<td>540.31</td>
<td>2058</td>
<td>13</td>
<td>18</td>
<td></td>
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</table>
frequencies, \(^6\text{--}^{18}\langle \nu_{\text{CO}} \rangle\). These values, also listed in Table I, were calculated from literature assignments of the frequencies by giving a weight of 1 to those of A or B symmetry, a weight of 2 to those of E symmetry, and a weight of 3 to those of T symmetry. A plot of \(E_B(0 \, 1s)\) vs \(\langle \nu_{\text{CO}} \rangle\), given in Figure 1, shows that these quantities are closely correlated. The straight line through the points corresponds to the equation \(E_B(0 \, 1s) = 0.0146 \langle \nu_{\text{CO}} \rangle + 510.00\). We believe that this correlation is strong evidence that both \(E_B(0 \, 1s)\) and \(\langle \nu_{\text{CO}} \rangle\) can be used to measure back-bonding in carbonyl complexes.

It is of considerable interest to know what structural and electronic factors are important in determining that one carbonyl has a large amount of back-bonding and that another has a relatively small amount of back-bonding. One would expect, other things being equal, that a low effective nuclear charge on the metal atom would be conducive to back-bonding. The effective nuclear charge of the metal atoms in carbonyl complexes probably increases fairly regularly as the position of the metal in the periodic table moves from left to right. Hence we can use \(n_v\), the number of valence electrons on the free metal atom, as a parameter linearly related to the effective nuclear charge of the metal in a carbonyl complex.

Another factor expected to influence the degree of back-bonding in a metal-carbon monoxide linkage is the competition for metal \(d\) electrons due to other carbonyl groups bonded to the metal, and due to other back-bonding ligands. The back-bonding in a carbonyl linkage should decrease with an increase in \(n_{\text{CO}}\), defined as the total number of coordinated carbonyl groups and groups equivalent to carbonyl groups. In the case of carbonyl complexes containing ligands other than \(\text{CO}\), we assume somewhat arbitrarily (although in fair agreement with prevailing opinions)
regarding the back-bonding abilities of ligands) that each of the following ligands is equivalent, as a $\pi$ acceptor, to one CO group: C$_7$H$_8$ (tetrahapto), C$_6$H$_5$, C$_5$H$_5$, C$_4$H$_6$, CH$_3$(OCH$_3$)C, SiCl$_3$. We also assume that the C$_7$H$_7$ ligand is equivalent to two CO's, that the CH$_3$CO ligand is equivalent to one-half CO, and that the H atom and CH$_3$ group have no $\pi$ acceptor character.

Back-bonding should decrease with an increase in either $n_v$ or $n_{\text{CO}}$. Although it is not clear that the terms should be weighted equally, we have used the simple sum, $(n_v + n_{\text{CO}})$, as a parameter which is expected to correlate with $E_B(0\ 1s)$ and $\langle \nu_{\text{CO}} \rangle$. The values of the parameter $(n_v + n_{\text{CO}})$ are given in Table I, and in Figure 2 is shown a plot of $E_B(0\ 1s)$ vs $(n_v + n_{\text{CO}})$. The plot shows that there is a definite correlation$^{22}$ between these quantities, and, although the correlation is not as good as that of Figure 1, the plot indicates that our ideas regarding the fundamental nature of back-bonding are qualitatively sound. The poor fit of the point for V(00)$^6$ is perhaps due to the fact that the vanadium atom in this compound is one electron short of the krypton effective atomic number. This electron deficiency would be expected to make the vanadium atom a relatively poor $d\pi$ donor.

When the appropriate XPS data become available, it will be of interest to test the correlations which we have observed with data for bridging carbonyl groups.

**Experimental Section**

All spectra were obtained with samples in the gas phase. Except in the case of Fe(CO)$_5$, the old Berkeley iron-free magnetic spectrometer and previously described procedures were used.$^{23,24}$ Differences between some of the data of Table I and previously published data are due to a spectrometer
recalibration and the present use of the value 248.62 eV for the Ar 2p\textsubscript{3/2} reference.\textsuperscript{25} The spectrum of Fe(CO)\textsubscript{5} was obtained using the Uppsala high resolution spectrometer;\textsuperscript{26} the O 1s binding energy was measured relative to that for CO, 542.57 eV. The binding energies given to two decimal places have probable errors of ±0.05 eV; those given to one decimal place have probable errors of ±0.1 eV.

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References and Notes


(2) G. M. Bodner, Paper No. 149, presented to the Division of Inorganic Chemistry at the Natl. A. C. S. Mtg., San Francisco, Fall 1976.


(19) Std. deviation = 0.20 eV; correlation coefficient = 0.940.
One thing assumed, inter alia, is that the compounds under consideration fulfill the 18-electron rule.


Correlation coefficient 0.81 including the V(CO)$_6$ point; 0.87 without the V(CO)$_6$ point.


Figure Captions

Figure 1. A plot of oxygen 1s binding energies for carbonyl complexes vs the multiplicity-weighted C-O stretching frequencies. Data given in Table I.

Figure 2. A plot of oxygen 1s binding energies for carbonyl complexes vs the parameter $(n_V + n_{CO})$. Data given in Table I.
Fig. 2
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