Title
ORBITALS AND HYPERCONJUGATION. AN X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY OF SOME ISOELECTRONIC COMPOUNDS

Permalink
https://escholarship.org/uc/item/5157q4r5

Authors
Avanzino, Steven C.
Jolly, William L.
Lazarus, Marc S.
et al.

Publication Date
1974-10-01
d ORBITALS AND HYPERCONJUGATION. AN X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY OF SOME ISOELECTRONIC COMPOUNDS

Steven C. Avanzino, William L. Jolly, Marc S. Lazarus, Winfield B. Perry, Richard R. Rietz, and Theodore F. Schaaf

October, 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

For Reference
Not to be taken from this room
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
-1-

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

d Orbitals and Hyperconjugation. An X-Ray Photoelectron Spectroscopic Study of Some Isoelectronic Compounds

Steven C. Avanzino, William L. Jolly,* Marc S. Lazarus, Winfield B. Perry, Richard R. Rietz, and Theodore F. Schaaf

ABSTRACT

The core electron binding energies of gaseous isoelectronic transition metal compounds show trends which differ from those of analogous isoelectronic nonmetal compounds. The data are consistent with the proposition that d orbitals are important in the bonding of transition metals but unimportant in the bonding of nonmetals. The data also suggest that hyperconjugation is important in nonmetal compounds when the process involves a shift of negative charge density to electronegative atoms.
We have measured core electron binding energies for the atoms in several sets of isoelectronic, isostructural compounds in the gas phase and have interpreted the data in terms of the nature of the chemical bonding in these compounds.

Consider the oxygen 1s and chlorine 2p$_{3/2}$ binding energies in Table I. Going from TiCl$_4$ to MnO$_3$Cl by the stepwise replacement of chlorine atoms by oxygen atoms and the simultaneous stepwise increase in the atomic number of the transition metal produces predictable changes in the atomic charges. From simple electronegativity considerations, one predicts that the process should be accompanied by an increase in the positive charge on the transition metal and a decrease in the negative charges on the oxygen and chlorine atoms. The data for TiCl$_4$, VOCl$_3$, CrO$_2$Cl$_2$, and MnO$_3$Cl are consistent with the prediction. However, because a core binding energy is influenced by both the charge on the atom which loses the core electron and by the charges on the other atoms of the molecule, one cannot be sure whether an increase in the oxygen or chlorine binding energy is due principally to the increase in the charge of the transition metal or to the decrease in the negative charge of the ligand atom itself.

The oxygen and chlorine binding energies for the short series from SiCl$_4$ to SO$_2$Cl$_2$, in Table I, and the oxygen and fluorine binding energies for the series from SiF$_4$ to ClO$_3$F, in Table II, show trends which differ from those of the corresponding data of the transition metal compounds. One difference is that the oxygen binding energy shifts are significantly greater in the compounds of the nonmetals. We believe that these greater shifts are due to the fact that the charge on the central atom increases much more in the nonmetal series than in the transition metal series. This
Table I. Oxygen 1s and Chlorine 2p3/2 Binding Energies

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_B$, eV 0 1s</th>
<th>$E_B$, eV Cl 2p3/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl4</td>
<td>538.73 &gt; 0.16</td>
<td>205.77 &gt; 0.16</td>
</tr>
<tr>
<td>VOCl₃</td>
<td>538.89 &gt; 0.54</td>
<td>206.01 &gt; 1.27</td>
</tr>
<tr>
<td>CrO₂Cl₂</td>
<td>539.43 &gt; 0.54</td>
<td>207.28 &gt; 1.27</td>
</tr>
<tr>
<td>MnO₃Cl</td>
<td></td>
<td>206.77 &gt; 0.39</td>
</tr>
<tr>
<td>SiCl₄</td>
<td>537.80 &gt; 1.54</td>
<td>207.16 &gt; 0.16</td>
</tr>
<tr>
<td>POCl₃</td>
<td>539.34 &gt; 1.54</td>
<td>207.32 &gt; 0.15</td>
</tr>
<tr>
<td>SO₂Cl₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table II. Oxygen 1s and Fluorine 1s Binding Energies

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_B$, eV 0 1s</th>
<th>$E_B$, eV F 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiF₄</td>
<td>538.9 &gt; 1.4</td>
<td>694.56 &gt; 0.8</td>
</tr>
<tr>
<td>POF₃</td>
<td>540.3 &gt; 0.7</td>
<td>695.4 &gt; 0.0</td>
</tr>
<tr>
<td>SO₂F₂</td>
<td>541.0 &gt; 0.7</td>
<td>695.4 &gt; -0.4</td>
</tr>
<tr>
<td>ClO₃F</td>
<td>694.0</td>
<td></td>
</tr>
<tr>
<td>SNF₃</td>
<td></td>
<td>695.0</td>
</tr>
</tbody>
</table>
result can be understood in terms of simple valence bond structures. The transition metal compounds, in which metal 3d orbitals are importantly involved in the bonding, can be represented by structures such as the following

\[ \begin{align*}
  &\text{Cl} \\
  &\text{O} \equiv \text{V} \equiv \text{Cl} \\
  &\text{Cl}
\end{align*} \]

\[ \begin{align*}
  &\text{Cl} \\
  &\text{O} \equiv \text{Cr} \equiv \text{O} \\
  &\text{Cl}
\end{align*} \]

The formal charges of all the atoms in such structures are zero, and consequently the various metal atoms do not differ greatly in charge. However, the nonmetal compounds, in which the 3d orbitals of the central atoms are not as importantly involved in the bonding, can be represented by structures such as the following

\[ \begin{align*}
  &\text{Cl} \\
  &\text{O} \equiv \text{P}^+ \equiv \text{Cl} \\
  &\text{Cl}
\end{align*} \]

\[ \begin{align*}
  &\text{Cl} \\
  &\text{O} \equiv \text{S}^{2+} \equiv \text{O} \\
  &\text{Cl}
\end{align*} \]

The formal charges of the central atoms increase with increasing atomic number (from zero in SiF$_4$ to 3+ in ClO$_3$F), and therefore the actual charges of the central atoms increase more than in the analogous transition metal compounds. We believe that the oxygen chemical shifts in the nonmetal series are primarily caused by changes in the coulombic potential, which is affected mainly by changes in the charge of the central atom.

Another difference between the transition metal and nonmetal compounds can be seen by comparing the chlorine binding energy shifts in the TiCl$_4$-MnO$_3$Cl series (Table I) with the fluorine binding energy shifts in the SiF$_4$-ClO$_3$F series.
(Table II). Whereas the chlorine binding energies increase continuously from TiCl$_4$ to MnO$_2$Cl, the fluorine binding energies increase between SiF$_4$ and POF$_3$, remain constant between POF$_3$ and SO$_2$F$_2$, and decrease between SO$_2$F$_2$ and ClO$_3$F. We believe the reversal of the trend in the fluorine binding energies is caused by an opposing trend in the fluorine atom charge. The trend due to the increasing charge of the central atom, which we have already discussed, dominates between SiF$_4$ and POF$_3$. We propose that the second trend, which dominates between SO$_2$F$_2$ and ClO$_3$F, is caused by an increase in the negative charge of the fluorine atom due to hyperconjugation. Hyperconjugation (sometimes called "no-bond resonance") corresponds to the contribution of resonance structures of the following type.

\[
\begin{array}{ccc}
\text{F} & \text{F} & \text{O}^-\\
\text{O}==\text{P}^+&\text{F} & \text{O}==\text{S}^{2+}&\text{O}^-\\
\text{F}^- & \text{F}^- & \text{O}==\text{Cl}^{3+}&\text{F}^-
\end{array}
\]

This type of bonding transfers some of the negative formal charge of oxygen atoms to fluorine atoms. On going from POF$_3$ to ClO$_3$F, the number of oxygen atoms which can transfer negative charge increases from one to three and the number of fluorine atoms which can accept negative charge decreases from three to one. Consequently the fluorine atoms acquire an increasing amount of negative formal charge in this series. The effect of the changing formal charge on the actual charge of the fluorine atoms is apparently most marked between SO$_2$F$_2$ and ClO$_3$F.

The compounds SiF$_4$, POF$_3$, and SNF$_3$ constitute an isoelectronic series formed by the hypothetical transfer of one, and then two, protons from one
of the fluorine atom nuclei of SiF₄ to the silicon nucleus. The amount of hyperconjugation would be expected to increase because of the decrease in electronegativity on going from F to O to N. The decrease in the fluorine binding energy between POF₃ and SNF₃ is consistent with this expectation.

Binding energies for another isoelectronic series of compounds, ranging from P(CH₃)₃BH₃ to P(CH₃)₃O, are given in Table III. Data for P(CH₃)₃ are included for comparison. The phosphorus binding energies for the tetracovalent compounds are considerably more positive than that for P(CH₃)₃; this result is expected because of the +1 formal charge on the phosphorus atoms of the tetracovalent compounds. Within the set of tetracovalent compounds, the phosphorus binding energies increase from P(CH₃)₃BH₃ to P(CH₃)₃O because of the increase in electronegativity on going from boron to oxygen. The carbon 1s binding energies for the methyl groups of tetracovalent compounds are slightly higher than that for P(CH₃)₃; this small difference is again probably attributable to the increased positive charge on the phosphorus atoms in the tetracovalent compounds and does not rule out the possibility that the methyl carbon atoms are more negative than those in P(CH₃)₃ because of hyperconjugation. The core binding energies of the boron, carbon, nitrogen and oxygen atoms in the groups BH₃, CH₂, NH, and O (each bonded to P(CH₃)₃) are, respectively, 192.76, 287.83, 402.38, and 535.88 eV. To our knowledge these binding energies are the lowest which have ever been recorded for these elements. It appears that hyperconjugation in this series of compounds is less pronounced than in the compounds of Table II.
### Table III. Phosphorus 2p3/2 and Carbon 1s Binding Energies

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_B$, eV</th>
<th>$E_B$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P 2p3/2</td>
<td>C 1s</td>
</tr>
<tr>
<td>P(CH₃)₃BH₃</td>
<td>137.00</td>
<td>290.79</td>
</tr>
<tr>
<td>P(CH₃)₃CH₂</td>
<td>137.03</td>
<td>290.40</td>
</tr>
<tr>
<td>P(CH₃)₃NH</td>
<td>137.39</td>
<td>290.63</td>
</tr>
<tr>
<td>P(CH₃)₃O</td>
<td>137.63</td>
<td>290.57</td>
</tr>
<tr>
<td>P(CH₃)₃</td>
<td>135.76</td>
<td>290.13</td>
</tr>
</tbody>
</table>
All in all, the data support the propositions that second-row nonmetallic elements do not accept more than four electron pairs in their valence shells and that hyperconjugation is significant when it involves a shift of negative charge density to electronegative atoms such as fluorine atoms.

Experimental Section

Some of the binding energies listed in Tables I, II, and III have been previously reported. All the data were obtained using the Berkeley iron-free spectrometer using techniques previously described. The uncertainty of values quoted to 0.1 eV is ±0.1 eV; that of values quoted to 0.01 eV is ±0.05 eV.

The TiCl$_4$ and Cr$_2$O$_2$Cl$_2$ were prepared by well-known methods; the measured boiling points (134 and 115°, resp.) agreed well with the published values (136.4 and 117°, resp.). The MnO$_3$Cl was prepared by the method of Briggs, taking care to maintain the reaction mixture below -45° to ensure the absence of other oxychlorides. The ClO$_3$F was synthesized by a literature procedure; its vapor pressure at -83° (88 Torr) agreed well with the published value (90 Torr). Commercial samples of VOCl$_3$ (0° vapor pressure 4.2 Torr; literature, 4.4 Torr) and SO$_2$Cl$_2$ (b.p. 69.5-70.0°; literature, 69.2°) were used.

Trimethylphosphine was prepared from PCl$_3$ and LiCH$_3$; its vapor pressure at 0° (156 Torr) agreed well with the literature values ranging from 154 to 161 Torr. Trimethylphosphine borane was prepared by the reaction of stoichiometric amounts of B$_2$H$_6$ and P(CH$_3$)$_3$. Trimethylphosphine methyldide was prepared by a modification of the procedure of Koester et al.
Tetramethylphosphonium iodide (10.3 g) was added under nitrogen to an excess of freshly precipitated KNaNH₂ dispersed in about 200 ml of triglyme. While the reaction mixture was refluxed, the product vapors were taken off under vacuum and allowed to pass through cold traps at -23°, -78°, and -196°. The P(CH₃)₃CH₂ (2.64 g) was obtained from the -78° trap. The mass spectrum had a parent peak at m/e = 90. The proton nmr spectrum of the neat product showed two doublets; one at δ = 0.7 with respect to TMS, J = 6 Hz (intensity 1), the other at δ = 1.38 with respect to TMS, J = 12 Hz (intensity 4.5). Trimethylphosphineimide was isolated in an attempt to prepare P(CH₃)₃CH₂ in liquid ammonia. Tetramethylphosphonium iodide (15.4 g) was added to 100 mmol of freshly precipitated KNaNH₂ in about 100 ml liquid ammonia. The reaction mixture was stirred for an hour, when the ammonia had evaporated. The volatile products were passed through cold traps at -23°, -78°, and -196°. An oily material which partially solidified upon standing and which evolved CH₄ was collected in the -23° and -78° traps. After two days, 0.28 g of P(CH₃)₃NH was sublimed from the traps, leaving a viscous, nonvolatile oily residue. The melting point (58°-59°) agreed with the literature¹⁵ and the mass spectrum showed a parent peak at m/e = 91 and a strong, pressure-dependent P + 1 peak. A proton nmr spectrum of the neat material showed a singlet at δ = 0.1 relative to TMS of intensity of 1, and a doublet at δ = 1.65 relative to TMS with J = 13 Hz and an intensity of 9. Trimethylphosphine oxide was prepared from POCl₃ and CH₂MgBr;¹⁶ its melting point (136°-138°) agreed with the literature.
Acknowledgments

This work was supported by the U. S. Atomic Energy Commission and the National Science Foundation (Grant GP-41661X). We are grateful to Mr. Thomas S. Briggs for preparing the MnO₃Cl.
References


(3) The formal charge is the charge which the atom would have if the bonding electrons in each bond were equally apportioned between the pair of bonded atoms.

(4) Admittedly formal charge is only a way to count the number of bonding and nonbonding electrons in a valence shell; however, other things being equal, an increase in formal charge is accompanied by an increase in atomic charge. For a quantitative relationship, see references 5 and 6.


(11) Ref. 10, p. 1265

(12) Ref. 10, p. 385.


This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.