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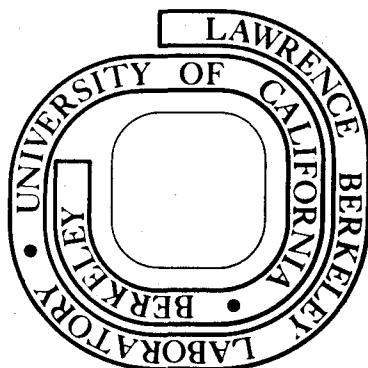
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Winfield B. Perry, Richard R. Rietz, and Theodore F. Schaaf

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d Orbitals and Hyperconjugation. An X-Ray Photoelectron Spectroscopic

Study of Some Isoelectronic Compounds

Steven C. Avanzino, William L. Jolly,* Marc S. Lazarus,

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ABSTRACT

The core electron binding energies of gaseous isoelectronic transition

metal compounds show trends which differ from those of analogous iso-

electronic 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_3Cl 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_2Cl_2, and MnO_3Cl 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,[1] 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_2Cl_2, in Table I, and the oxygen and fluorine binding energies for the series from SiF_4 to ClO_3F, 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 $2p_{3/2}$ Binding Energies

Compound	E_B, eV 0 1s	E_B, eV Cl $2p_{3/2}$
$TiCl_4$		205.77 ⟩ 0.16
$VOCl_3$	538.73 ⟩ 0.16	205.93 ⟩ 0.08
CrO_2Cl_2	538.89 ⟩ 0.54	206.01 ⟩ 1.27
MnO_3Cl	539.43	207.28
$SiCl_4$		206.77 ⟩ 0.39
$POCl_3$	537.80 ⟩ 1.54	207.16 ⟩ 0.16
SO_2Cl_2	539.34	207.32

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

Compound	E_B, eV 0 1s	E_B, eV F 1s
SiF_4		694.56 ⟩ 0.8
POF_3	538.9 ⟩ 1.4	695.4 ⟩ 0.0
SO_2F_2	540.3 ⟩ 0.7	695.4 ⟩ -0.4
ClO_3F	541.0	694.0
SNF_3		695.0

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

$$O=V-Cl \quad\text{with}\quad Cl \text{ above and } Cl \text{ below} \qquad O=Cr=O \quad\text{with}\quad Cl \text{ above and } Cl \text{ below}$$
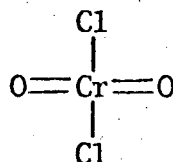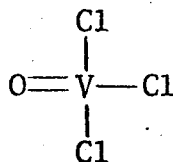
The formal charges of all the atoms in such structures are zero, and consequently the various metal atoms do not differ greatly in charge. Howeve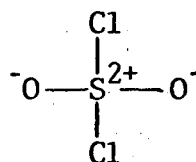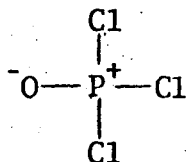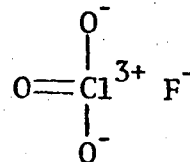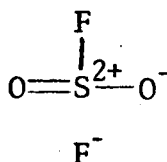r, the nonmetal compounds, in which the 3d orbitals of the central atoms are not as importantly involved in the bonding,[2] can be represented by structures such as the following

$$^-O-P^+-Cl \quad\text{with}\quad Cl \text{ above and } Cl \text{ below} \qquad ^-O-S^{2+}-O^- \quad\text{with}\quad Cl \text{ above and } Cl \text{ below}$$

The formal charges[3] of the central atoms increase with increasing atomic number (from zero in SiF_4 to 3+ in ClO_3F), and therefore the actual charges of the central atoms increase more than in the analogous transition metal compounds.[4-6] 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_3Cl series (Table I) with the fluorine binding energy shifts in the SiF_4-ClO_3F series

(Table II). Whereas the chlorine binding energies increase continuously
from $TiCl_4$ to MnO_3Cl, the fluorine binding energies increase between
SiF_4 and POF_3, remain constant between POF_3 and SO_2F_2, and decrease between
SO_2F_2 and ClO_3F. 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_2F_2 and ClO_3F, 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.

$$
\begin{array}{ccc}
\overset{\textstyle F}{\underset{\textstyle F^-}{O \!=\!\! P^+ \!\!-\! F}} &
\overset{\textstyle F}{\underset{\textstyle F^-}{O \!=\!\! S^{2+} \!\!-\! O^-}} &
\overset{\textstyle O^-}{\underset{\textstyle O^-}{O \!=\!\! Cl^{3+} \; F^-}}
\end{array}
$$
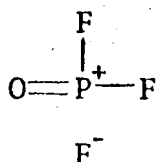
This type of bonding transfers some of the negative formal charge of
oxygen atoms to fluorine atoms. On going from POF_3 to ClO_3F, the number
of oxygen atoms which can transfer negative charge increases from one to
three and the number of fluorine atoms which can accept negative charge
decreases from 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_2F_2 and ClO_3F.

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 SiF_4 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 POF_3 and SNF_3 is consistent with this expectation.

Binding energies for another isoelectronic series of compounds, ranging from $P(CH_3)_3BH_3$ to $P(CH_3)_3O$, are given in Table III. Data for $P(CH_3)_3$ are included for comparison. The phosphorus binding energies for the tetracovalent compounds are considerably more positive than that for $P(CH_3)_3$; 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 $P(CH_3)_3BH_3$ to $P(CH_3)_3O$ because of the increase in electronegativity on going from boron to oxygen. The carbon 1s binding energies for the methyl groups of the tetracovalent compounds are slightly higher than that for $P(CH_3)_3$; 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 $P(CH_3)_3$ because of hyperconjugation. The core binding energies of the boron, carbon, nitrogen and oxygen atoms in the groups BH_3, CH_2, NH, and O (each bonded to $P(CH_3)_3$) 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 $2p_{3/2}$ and Carbon 1s Binding Energies

Compound	E_B, eV $P\ 2p_{3/2}$	E_B, eV $C\ 1s$
$P(CH_3)_3BH_3$	137.00	290.79
$P(CH_3)_3CH_2$	137.03	290.40
$P(CH_3)_3NH$	137.39	290.63
$P(CH_3)_3O$	137.63	290.57
$P(CH_3)_3$	135.76	290.13

. 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 $TiCl_4$[7] and CrO_2Cl_2[8] 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_3Cl was prepared by the
method of Briggs,[9] taking care to maintain the reaction mixture below -45°
to ensure the absence of other oxychlorides. The ClO_3F was synthesized
by a literature procedure;[10] 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,[11] 4.4 Torr) and SO_2Cl_2
(b.p. 69.5-70.0°; literature,[12] 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.[13] Trimethylphosphine borane was prepared by the reaction of
stoichiometric amounts of B_2H_6 and $P(CH_3)_3$. Trimethylphosphine methylide
was prepared by a modification of the procedure of Koester et al.[14]

Tetramethylphosphonium iodide (10.3 g) was added under nitrogen to an excess of freshly precipitated KNH_2 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 $P(CH_3)_3CH_2$ (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 $\delta = -0.7$ with respect to TMS, $J = 6Hz$ (intensity 1), the other at $\delta = 1.38$ with respect to TMS, $J = 12Hz$ (intensity 4.5). Trimethylphosphineimide was isolated in an attempt to prepare $P(CH_3)_3CH_2$ in liquid ammonia. Tetramethylphosphonium iodide (15.4 g) was added to 100 mmol of freshly precipitated KNH_2 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 CH_4 was collected in the $-23°$ and $-78°$ traps. After two days, 0.28 g of $P(CH_3)_3NH$ was sublimed from the traps, leaving a viscous, nonvolatile oily residue. The melting point ($58°-59°$) agreed with the literature[15] 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 $\delta = 0.1$ relative to TMS of intensity of 1, and a doublet at $\delta = 1.65$ relative to TMS with $J = 13Hz$ and an intensity of 9. Trimethylphosphine oxide was prepared from $POCl_3$ and CH_3MgBr;[16] its melting point ($136°-138°$) agreed with the literature.

Acknowledgments

-11-

References

(1) Discussions of the electrostatic "potential term" in the calculation of core binding energies from atomic charges are found in K. Siegbahn et al., "ESCA Applied to Free Molecules," North-Holland Publ. Co, Amsterdam, 1969 and U. Gelius, Physica Scripta, 9, 133 (1974).

(2) T. B. Brill, J. Chem. Education, 50, 392 (1973).

(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.

(5) W. L. Jolly and W. B. Perry, J. Amer. Chem. Soc., 95, 5442 (1973).

(6) W. L. Jolly and W. B. Perry, Inorg. Chem., in press.

(7) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1970, pp. 453-456.

(8) H. H. Sisler, Inorg. Syn., 2, 205 (1946).

(9) T. S. Briggs. J. Inorg. Nucl. Chem., 30, 2866 (1968).

(10) G. Brauer, "Handbook of Preparative Inorganic Chemistry," 2nd ed., Academic Press, New York, 1963, p. 166.

(11) Ref. 10, p. 1265

(12) Ref. 10, p. 385.

(13) R. Thomas and K. Eriks, Inorg. Syn., 9, 59 (1967).

(14) R. Koester, D. Simie, M. A. Grassberger, Liebigs Ann. Chem., 739, 211 (1970).

(15) C. Screttas and A. F. Isbell, J. Org. Chem., 27, 2573 (1962).

(16) A. B. Burg and W. E. McKee, J. Amer. Chem. Soc., 73, 4590 (1951).

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