(7) D. J. Miller and L. C. Cusachs, *Jerusalem Symp. Quantum Chem. Biochem.*, **2**, 276–283 (1972).
(8) W. W. Fogleman, D. J. Miller, H. B. Jonassen, and L. C. Cusachs, *Inorg. Chem.*, **8**, 1209 (1969).
(9) F. Tuinstra, *J. Chem. Phys.*, **46**, 2741 (1967).
(10) J. A. Semlyen, *Trans. Faraday Soc.*, **63**, 743 (1967).
(11) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.
(12) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).
(13) D. P. Santry, *J. Am. Chem. Soc.*, **90**, 3309 (1968).
(14) J. R. Sabin, D. P. Santry, and K. Weiss, *J. Am. Chem. Soc.*, **94**, 6651 (1972).
(15) D. B. Chesnut and P. E. S. Wormer, *Theor. Chim. Acta*, **20**, 250 (1971).
(16) J. Donohue, A. Caron, and E. Goldish, *J. Am. Chem. Soc.*, **83**, 3748 (1961).
(17) G. Klopman and B. O'Leary, "All Valence Electrons S.C.F. Calculations", Springer-Verlag, Berlin, 1970.
(18) J. N. Lyness and C. B. Moler, *Numer. Math.*, **8**, 458 (1966).
(19) The energy minima were obtained by quadratically fitting the points for three bond angles (98.2, 102.2, and 106.2°) which define shallow portions of potential curves (depth <3 kcal/mol in all cases). For the boat form, the results of separate sets of calculations with α_1 and α_2

(20) A. Veillard and J. Demuynck, *Chem. Phys. Lett.*, **4**, 476 (1970).
(21) M. E. Schwartz, *J. Chem. Phys.*, **51**, 4182 (1969).
(22) For a recent review of the conformational aspects of six-membered rings, see G. M. Kellie and F. G. Riddell, *Top. Stereochem.*, **8**, 225–269 (1974).
(23) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *J. Am. Chem. Soc.*, **90**, 1199 (1968).
(24) J. R. Hoyland, *J. Chem. Phys.*, **50**, 2775 (1969).
(25) A. D. Walsh, *J. Chem. Soc.*, 2260, 2266, 2268, 2296, 2301, 2306 (1953).
(26) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1970.
(27) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1948, p 189.
(28) L. M. Sachs, M. Geller, and J. J. Kaufman, *J. Chem. Phys.*, **51**, 2771 (1969).
(29) W. Giordano, J. R. Hamann, J. J. Harkins, and J. J. Kaufman, *Mol. Pharmacol.*, **3**, 307 (1967).
(30) P. D. Bartlett, R. E. Davis, and E. F. Cox, *J. Am. Chem. Soc.*, **83**, 103 (1961).
(31) G. Nickless, "Inorganic Sulfur Chemistry", Elsevier, Amsterdam, 1968, pp 246, 351.

Evidence for Hyperconjugation from an X-Ray Photoelectron Spectroscopic Study of Isoelectronic Compounds

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The shifts in core electron binding energies of oxygen, chlorine, and carbon atoms in some gaseous isoelectronic isostructural compounds can be readily explained in terms of simple trends in atomic charges. However the fluorine 1s binding energies for some fluoro compounds of silicon, phosphorus, sulfur, and chlorine show unusual shifts which suggest that hyperconjugation is important in the bonding of these compounds.

We have measured atomic core electron binding energies for several series of isoelectronic, isostructural compounds in the gas phase. Isoelectronic compounds were chosen for study because of the probability that the nature of the bonding in such compounds changes in a fairly systematic way with changes in the atomic numbers of the atoms in a given series of compounds. A core binding energy can be accurately represented as a linear function of three quantities: the atomic charge, the electrostatic potential due to the other atoms of the molecule, and the electronic relaxation energy.[1] To a good approximation, the electronic relaxation energy for an atom of a particular element in a series of isoelectronic, isostructural compounds can be assumed to be constant.[2] Therefore chemical shifts in binding energy can be ascribed to changes in atomic charge and changes in potential. We shall make minimal use of estimated atomic charges in our interpretations; hence our conclusions should be relatively free of the weaknesses and assumptions of theoretical methods for estimating atomic charges.

Consider the tetracovalent phosphorus compounds listed in Table I. We may imagine this series of compounds to be generated by the stepwise transfer of the three protons in the BH_3 group of $P(CH_3)_3 \cdot BH_3$ to the boron nucleus of that molecule. Each step increases the electronegativity of the group attached to the $P(CH_3)_3$ group and causes the atomic charge of the phosphorus atom to increase. The effect of this trend in atomic charges can be seen in the phosphorus $2p_{3/2}$ binding energies, which increase on going from $P(CH_3)_3 \cdot BH_3$ to $P(CH_3)_3O$. The methyl groups are relatively remote from the changing atoms; hence the corresponding carbon 1s binding energies are less affected, and no significant trend in their values can be seen.

Table I. Phosphorus $2p_{3/2}$ and Carbon 1s Binding Energies

	E_B, eV	
Compd	P $2p_{3/2}$	C 1s
$P(CH_3)_3 \cdot BH_3$	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

Next consider the five series of isoelectronic compounds listed in Table II. In the first four series, halogen atoms or methyl groups are replaced stepwise with oxygen atoms as the atomic number of the central atom is increased stepwise. The last series of compounds may be looked upon as the compounds generated by the stepwise transfer of protons from one of the fluorine nuclei of SiF_4 to the silicon nucleus of that molecule. We believe it is reasonable to assume that, on progressing down through any one of the five series, the charge of the central atom increases.[3] This increase in charge, coupled with the decrease in size, of the central atom would be expected to cause increased electron withdrawal from a given type of ligand atom. Hence the increase in the charge of the central atom is probably responsible for the observed corresponding increase in the oxygen, chlorine, and carbon binding energies within each series.
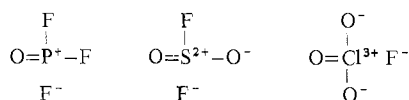
Notice, however, that the fluorine 1s binding energies do not follow the simple predicted trend. In both the fourth and fifth series, the fluorine 1s binding energies increase to a maximum value and then decrease. We believe that the increase between SiF_4 and POF_3 is caused by the dominating effect of the increased positive charge and electronegativity of the central atom. The decrease in fluorine binding energy between SO_2F_2 and ClO_3F and between POF_3 and SNF_3 is

Table II. Oxygen 1s, Chlorine 2p$_{3/2}$, Carbon 1s, and Fluorine 1s Binding Energies

Compd	E_B, eV			
	O 1s	Cl 2p$_{3/2}$	C 1s	F 1s
TiCl$_4$		205.77 }0.16		
VOCl$_3$	538.73 }0.16	205.93 }0.08		
CrO$_2$Cl$_2$	538.89	206.01 }1.27		
MnO$_3$Cl	539.43 }0.54	207.28		
SiCl$_4$		206.77 }0.39		
POCl$_3$	537.80 }1.54	207.16 }0.16		
SO$_2$Cl$_2$	539.34	207.32		
Si(CH$_3$)$_4$			289.61 }0.96	
P(CH$_3$)$_3$O	535.88 }1.79		290.57 }1.01	
S(CH$_3$)$_2$O$_2$	537.67		291.58	
SiF$_4$				694.56 }0.8
POF$_3$	538.9 }1.4			695.4 }0.0
SO$_2$F$_2$	540.3			695.4 }-1.2
ClO$_3$F	541.1 }0.8			694.2
SiF$_4$				694.56 }0.8
POF$_3$				695.4 }-0.4
SNF$_3$				695.0

apparently due to an increase in the negative charge of the fluorine atoms. This increase in negative charge tends to decrease the binding energy; clearly this effect is greater than and opposed to the effect of the increase in potential caused by the increase in positive charge on the central atom.

We believe that the increase in the negative charge of the fluorine atoms is due to the dominating effect of a large increase in the extent of hyperconjugation. Hyperconjugation (sometimes called "no-bond resonance") corresponds to the contribution of resonance structures of the three types shown.
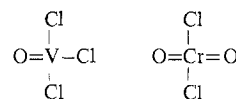
$$
\begin{array}{ccc}
\overset{\displaystyle F}{\underset{\displaystyle F^-}{O=P^+-F}} & \overset{\displaystyle F}{\underset{\displaystyle F^-}{O=S^{2+}-O^-}} & \overset{\displaystyle O^-}{\underset{\displaystyle O^-}{O=Cl^{3+}\ F^-}}
\end{array}
$$

This type of bonding transfers some of the negative formal charge[4] 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 1 to 3 and the number of fluorine atoms which can accept negative charge decreases from 3 to 1. Consequently, the fluorine atoms acquire an increasing amount of negative formal charge in this series. The effect of the changing formal charge of the actual charge of the fluorine atoms is apparently most marked between SO$_2$F$_2$ and ClO$_3$F. On going from POF$_3$ to SNF$_3$, the amount of hyperconjugation increases markedly because of the increased donor character (decreased electronegativity) of the nitrogen atom compared with that of the oxygen atom. The decrease in the fluorine binding energy, corresponding to more negatively charged atoms, is consistent with the increased hyperconjugation.

The fact that the effect of hyperconjugation on atomic charges is more apparent in the fluorine compounds than in the chlorine and methyl compounds is undoubtedly due to the greater electronegativity of fluorine atoms and the corresponding greater ability of fluorine atoms to accept negative charge. It is possible that hyperconjugation occurs even in methyl compounds such as P(CH$_3$)$_3$O and S(CH$_3$)$_2$O$_2$ but that the effect is not strong enough to cause a reversal in the carbon binding energies like that observed in the fluorine binding energies.

If one accepts the possibility of 2pπ→3dπ bonding between the oxygen atoms and the central atoms of the fluorine compounds, the decrease in the fluorine binding energy on going from SO$_2$F$_2$ to ClO$_3$F might be explained by decreasing positive charge on the central atom due to increased pπ→dπ bonding. However, there are two arguments against this

alternative explanation. (1) Because of electron repulsions on the central atom, the increase in 3d electron density in the SiF$_4$–ClO$_3$F series would be expected to be greatest between SiF$_4$ and POF$_3$ and least between SO$_2$F$_2$ and ClO$_3$F. (2) The shifts in the oxygen 1s binding energies of the transition metal compounds (VOCl$_3$–MnO$_3$Cl) are appreciably smaller than those of the nonmetal compounds. The transition metal compounds, in which metal 3d orbitals are importantly involved in the bonding, can be represented by structures such as the two shown for V and Cr, in which the formal charges of the metal atoms are zero. If structures analogous to these were

$$
\begin{array}{cc}
\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{O=V-Cl}} & \overset{\displaystyle Cl}{\underset{\displaystyle Cl}{O=Cr=O}}
\end{array}
$$

important in the nonmetal compounds, the oxygen chemical shifts for those compounds would probably be smaller than they actually are.

Experimental Section

Some of the binding energies listed in Tables I and II have been previously reported.[5] All the data were obtained with the Berkeley iron-free spectrometer using techniques previously described.[6] The precision of most of the binding energies, as established by two or three measurements on different samples, is ±0.05 eV or better. These binding energies are quoted to 0.01 eV. The values quoted to 0.1 eV are believed to be reliable to ±0.1 eV. Changes in the chemical shifts of 0.1 eV would not cause any changes in our interpretation. Comparison of other binding energy data with data for the same compounds obtained in other laboratories indicates that the absolute accuracy of our data is about ±0.2 eV or better.

TiCl$_4$[7] and CrO$_2$Cl$_2$[8] were prepared by well-known methods; the boiling points measured at approximately 755 Torr (134 and 115°, respectively) agreed well with the published values of the normal boiling points (136.4 and 117°, respectively). MnO$_3$Cl 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$_3$F 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; lit.[11] 4.4 Torr) and SO$_2$Cl$_2$ (bp at atmospheric pressure 69.5–70.0°; lit.[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$_2$H$_6$ and P(CH$_3$)$_3$. Trimethylphosphinemethylide was prepared by a modification of the procedure of Koester et al.[14] Tetramethylphosphonium iodide (10.3 g) was added under nitrogen to freshly precipitated KNH$_2$ (in about

25% excess) 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 δ -0.7 with respect to TMS, $J = 6$ Hz (intensity 1), and the other at δ 1.38 with respect to TMS, $J = 12$ Hz (intensity 4.5). Trimethylphosphineimide was isolated in an attempt to prepare $P(CH_3)_3CH_2$ in liquid ammonia. Tetramethylphosphonium iodide (15.4 g) was added to 100 mmol of freshly precipitated KNH_2 in about 100 ml of liquid ammonia. The reaction mixture was stirred for 1 hr 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 2 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 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 $POCl_3$ and CH_3MgBr;[16] its melting point ($136-138°$) agreed with the literature value ($137.5-138.5°$).

Registry No. $P(CH_3)_3 \cdot BH_3$, 1898-77-7; $P(CH_3)_3CH_2$, 14580-91-7; $P(CH_3)_3NH$, 15107-02-5; $P(CH_3)_3O$, 676-96-0; $TiCl_4$, 7550-45-0; $VOCl_3$, 7727-18-6; CrO_2Cl_2, 7791-14-2; MnO_3Cl, 15605-27-3; $SiCl_4$, 10026-04-7; $POCl_3$, 10025-87-3; SO_2Cl_2, 7791-25-5; $Si(CH_3)_4$, 75-76-3; $S(CH_3)_2O_2$, 67-71-0; SiF_4, 7783-61-1; POF_3, 13478-20-1; SO_2F_2, 2699-79-8; ClO_3F, 7616-94-6; SNF_3, 15930-75-3; KNH_2, 17242-52-3; tetramethylphosphonium iodide, 993-11-3.

References and Notes

(1) U. Gelius, *Phys. Scr.*, **9**, 133 (1974).
(2) The following references provide evidence that the relaxation energy associated with the core ionization of an atom is closely related to the number and types of atoms bonded to the atom: D. W. Davis and D. A. Shirley, *Chem. Phys. Lett.*, **15**, 185 (1972); W. L. Jolly and W. B. Perry, *J. Am. Chem. Soc.*, **95**, 5442 (1973).
(3) This assumption is obviously justified for the methyl and chlorine compounds, in which an increase in the nuclear charge of the central atom is accompanied by an increase in the electronegativity of one of the ligand atoms. The justification is not obvious in the case of the fluorine compounds unless one assumes that transfer of a proton from the nucleus of one atom to that of a second atom is accompanied by the transfer of less than a full electron to the second atom. However, various charge calculation methods (CNDO, extended Hückel, and electronegativity based) show that the assumption is valid for all the compounds in Table II.
(4) 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.
(5) W. L. Jolly and W. B. Perry, *Inorg. Chem.*, **13**, 2686 (1974).
(6) W. B. Perry and W. L. Jolly, *Inorg. Chem.*, **13**, 1211 (1974).
(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. Synth.*, **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, N.Y., 1963, p 166.
(11) Reference 10, p 1265.
(12) Reference 10, p 385.
(13) R. Thomas and K. Eriks, *Inorg. Synth.*, **9**, 59 (1967).
(14) R. Koester, D. Simie, and M. A. Grassberger, *Justus 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. Am. Chem. Soc.*, **73**, 4590 (1951).

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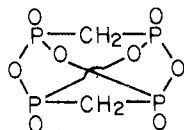
Full Anhydrization of Methylenediphosphonic Acid and of Phosphoric Acids by a Carbodiimide

THOMAS GLONEK, JOHN R. VAN WAZER,* and TERRELL C. MYERS

Methylenediphosphonic acid may be condensed by dicyclohexylcarbodiimide through a number of intermediate species to a compound identified by ^{31}P NMR as the unionized birdcage anhydride

which is a phosphonic analog of phosphorus pentoxide. The intermediate molecular species have been identified and the course of the reaction has been studied and discussed. As part of this work, we also have been able to condense various phosphoric acids to what appears to be a carbodiimide adduct of the birdcage P_4O_{10} molecule.

Introduction

A considerable body of evidence[1-6] has been developed to show that, under the usual laboratory conditions, esterifications of phosphoric acids and their esters (both simple and biological) mediated by carbodiimides and related condensing agents do not occur in the presence of an amine base whereas P–O–P condensation of these acids and esters proceeds readily under these conditions. However, in a study[7] from our group, it was shown that, in spite of this well-accepted conclusion, methylenediphosphonic acid—a close analog of pyrophosphoric acid—was easily esterified by isopropylidineadenosine to make the methylene-bridged analog of adenosine diphosphate, ADP, in high yield. Because of this finding, it seemed desirable to

investigate the fundamental inorganic chemistry of the carbodiimide-induced condensation of the simple methylenediphosphonic acid [(HO)$_2$(O)P]$_2$CH$_2$. In this work, described herein, we found that the condensation could be driven to completion, with all possible anhydride linkages being made. This emboldened us to attempt the synthesis of the P_4O_{10} molecule by a chemical condensation in solution of a simple phosphoric acid. Up to now, there has been no evidence for condensation of any phosphoric acid all the way to phosphoric anhydride and the dissolution of phosphorus pentoxide in a solvent has always (or almost always[8]) led to scission of P–O–P linkages.

Experimental Section

Crystalline methylenediphosphonic acid was prepared according to the literature[7,9] and all other reagents were purchased commercially.

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