factor was obtained for oxygen. The assumption of 90% order in the perovskite structure yielded R = 0.066. Thus a significantly lower discrepancy index was obtained for the complete ordering of the B and B′ ions in the perovskite structure.

Because the high-temperature structure is cubic, there is no distortion of the oxygen octahedra. However, the oxygen octahedra around the rare earth ion and the molybdenum ion are quite different in size. In the former the edge, O–O, is 3.39 Å while in the latter it is 2.63 Å. The oxygen–rare earth bond distance, 2.40 Å, is equal to the sum of the ionic radii of oxygen (1.40 Å) and neodymium (1.00 Å) whereas the oxygen–molybdenum bond distance, 1.86 Å, is about 0.2 Å less than the ionic bond distance, 2.03 Å.[11] Such a short distance would indicate strong covalent bonding between the molybdenum and oxygen atoms and therefore large overlap of the oxygen orbitals and the 4d orbitals of molybdenum. The distance found here corresponds to one of the Mo–O distances observed in $MoO[(S_2COC_2H_5)_2]_2O$[12] and a bond order of about 1.6 can be assigned to it.[13]

The molybdenum radius determined in this compound is 0.46 Å (O_2 radius 1.40 Å), and since the exact oxidation state is unknown, this is an average value for a mixture of the tetra-, penta-, and hexavalent ions. The Mo^{6+} radius in Ba_2CaMoO_6 can be calculated from the lattice constant a = 8.355 Å[14] and is 0.38 Å. The Mo^{6+} value is expected to be smaller although it is usually listed as 0.60 Å.[11] In $NaMoF_6$[15] the radius derived for Mo^{5+}, on the basis of the reported lattice constant, a = 8.194 Å, $r(Na^+)$ = 1.02 Å, and $r(F^-)$ = 1.33 Å, is 0.42 Å in closer agreement with the value found here. Perhaps the only conclusion that can be reached is that there is considerable uncertainty regarding the values for Mo radii which can be used, *a priori*, for predicting lattice constants of compounds containing this element.

From the studies of the stoichiometry of these materials it is likely that the single crystal contained Mo^{5+} and Mo^{6+}, and cation vacancies are most likely present in the unit cell. The rather high value of the oxygen temperature factor might be indicative of some disorder in the B sites and provides additional supportive evidence for the postulated nonstoichiometry of these materials.

[11] R. D. Shannon and C. D. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).

[12] A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Amer. Chem. Soc.*, **86**, 3024 (1964).

[13] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 867 (1965).

[14] E. G. Steward and H. P. Rooksby, *Acta Crystallogr.*, **4**, 503 (1951).

[15] A. J. Edwards and E. F. Peacock, *J. Chem. Soc.*, 4253 (1961).

CONTRIBUTION FROM THE DEPARTMENTS OF PHYSICS AND CHEMISTRY,
VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE 37203

π-Bond Feedback Interpreted from the Binding Energy of the "2p" Electrons[1] of Phosphorus

BY WAYNE E. MORGAN, WOJCIECH J. STEC, ROYAL G. ALBRIDGE, AND JOHN R. VAN WAZER*[2]

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The binding energies of the "2p" electrons[1] of phosphorus in 17 compounds were measured by means of X-ray photoelectron spectroscopy. In addition, where appropriate, the binding energies of the "1s" electrons of oxygen, the "2p" electrons of sulfur, and the "3p" electrons of selenium are also reported. The main part of this study involved comparison of the series of compounds having the structure R_3PM, where M stands for (a) the electron pair, (b) oxygen, (c) sulfur, and (d) selenium, with R being the phenyl group and, for structures b through d, the phenoxyl group. In the case of the first series (R = phenyl), data were also obtained on complexes with mercuric iodide. When going from oxygen to sulfur to selenium, there is essentially no change in the "2p"-binding energy and this is attributed to charge equalization through π-bond feedback. Several theoretical calculations, as well as an interpretation of ^{31}P nuclear magnetic resonance chemical shifts, are given to support this contention.

The phenomenon of p_π–d_π bonding has long been a subject of interest and dispute in the chemistry of phosphorus and other second-row elements. X-Ray photoelectron spectroscopy[3-5] of electrons in inner-shell orbitals seems to be a useful tool[3,6] for estimating the variation in the "charge" of an atom from one molecule to another and hence ought to be appropriate for evaluating p_π–d_π bonding. In this work, we shall assume that the inner-electron binding energies obtained from exciting a mass of molecular crystals are at least qualitatively interpretable in terms of the electronic structure of the isolated molecule.[6]

Experimental Section

The photoelectron spectrometer used in this work is a scaled-up version (35-cm radius) of a unit previously described[7] and the operation of the instrument, which is kept in an iron-free room, is controlled by a small computer.[8] This spectrometer has been

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[1] The designation of the atomic orbital for which a binding energy is measured is put in quotation marks; *e.g.*, "2p," since the inner orbitals of molecules are somewhat delocalized and hence are not identical with the corresponding atomic inner orbitals.

[2] To whom requests for reprints should be addressed.

[3] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, *Nova Acta Regiae Soc. Sci. Upsal.*, [4] **20**, 1 (1967).

[4] R. G. Albridge in "Physical Methods of Chemistry," Vol. II, A. Weissberger and B. W. Rossiter, Ed., Interscience, New York, N. Y., in press.

[5] J. M. Hollander and W. L. Jolly, *Accounts Chem. Res.*, **3**, 193 (1970).

[6] R. Nordberg, H. Brecht, R. G. Albridge, A. Fahlman, and J. R. Van Wazer, *Inorg. Chem.*, **9**, 2469 (1970).

[7] R. Nordberg, J. Hedman, P. F. Hedén, C. Nordling, and K. Siegbahn, *Ark. Fys.*, **37**, 489 (1968).

[8] A. Fahlman, R. G. Albridge, R. Nordberg, and W. M. LaCasse, *Rev. Sci. Instrum.*, **41**, 596 (1970).

shown to give values for binding energies which are consistent with those measured on other independently calibrated spectrometers.

The data reported here were obtained with the aluminum Kα X-ray line as the excitation source and the "1s" binding energy of the carbon present in the compound under study was employed as an "internal" reference line in the spectra. Although the use of an internal reference is generally unsuitable for photoelectron spectroscopy, we believe that for the compounds studied herein the measured carbon "1s" binding energy always appears at 285.0 eV (using $\beta\rho$ = 116.780 G cm).[9] This contention is made on the basis that aliphatic and aromatic carbons both exhibit this binding energy and that a single substitution on a benzene ring has an appreciable effect only on the substituted carbon atom,[10] with the remaining five carbons strongly dominating the resulting carbon "1s" peak and thereby holding the measured binding energy at 285.0 eV. The fact that, in Table I, trioctylphosphine oxide is indistinguishable from triphenylphosphine oxide is consistent with the above reasoning. It should be noted that the presence of other selenium lines (probably Auger) in the energy region of the selenium "3p" photoelectron line caused difficulties in measuring the latter.

All of the samples studied were crystalline materials exhibiting the proper melting points. They were either prepared by accepted procedures reported in the literature[11-14] or taken from our collection of chemicals. All samples were recrystallized from an inert solvent several times to ensure good purity. The selenium derivatives were protected from light to avoid photochemical decomposition. The sources for use in the spectrometer were prepared by heavily spreading the finely ground crystals onto ordinary "Scotch" brand tape. The thick layer of sample eliminated any appreciable carbon "1s" contribution from the adhesive backing.

Results

Measured Binding Energies.—The data obtained on the 17 samples studied are reported in Table I. These data include information about the "2p" orbital of phosphorus for all compounds, and, where appropriate, data are given for the "1s" orbital of oxygen, the "2p" orbital of sulfur, and the "3p" orbital of selenium. The ± numbers shown behind the average value for each set of measurements correspond to the respective standard deviations of the replicate determinations. On an absolute-energy scale, the error limits are larger than some of these deviations between replicates. This is due to the inclusion of uncertainties in such factors as the energy of the X-ray source, the energy of the calibration line, and the spectrometer work function[15] so that the absolute standard deviation of the measurements is about ±0.5 eV.

Five of the compounds listed in Table I have been measured by other investigators[16,17] and their results are also reported in the table. Since this study is dependent on small differences between the various binding energies, we felt it necessary to repeat the measurements on these five compounds to be sure that they could be properly compared to our other data. It should be noted that the agreement between our values and those of the previous workers is quite good.[18] Prior work[16] has shown that the overall range of phosphorus "2p" binding energies is rather large, covering nearly 9 eV, so that, when there is little difference between the binding energies of dissimilar compounds, an explanation must be sought.

Inspection of Table I shows that the aliphatic and aromatic phosphine oxides $(C_8H_{17})_3PO$ and $(C_6H_5)PO$ exhibit the same binding energy within experimental error. For the triphenyl compounds $(C_6H_5)_3PM$ there is an increase of *ca.* 1.6 eV in binding energy when going from M = the unshared pair of electrons to M = O, S, or Se. This value is very much less than the difference of 4.1 eV between the binding energies[3] of $(CH_3)_3$-NO at 402.2 eV and $(C_4H_9)_3N$ at 398.1 eV. Further, the binding energies of the three $(C_6H_5)_3PM$ compounds, for which M = O, S, or Se, are the same within experimental error. Likewise, for the triphenoxyl compounds $(C_6H_5O)_3PM$ the binding energies for M = O, S, or Se were found to be indistinguishable.

When mercury complexes were made by donating the unshared pair of electrons on $(C_6H_5)_3P$ to the Hg atom, there was essentially no change in the binding energy of the phosphorus "2p" electrons, probably indicating a balance between the effect on this energy of losing σ electrons and the effect of gaining π electrons on the phosphorus. For $(C_6H_5)_3PO$, complexing of the mercury through the phosphoryl oxygen also causes no detectable change in the phosphorus "2p" binding energy. However, in the case of $(C_6H_5)_3PS$ and perhaps $(C_6H_5)_3PSe$, complexing through the sulfur (or selenium) leads to a drop in the phosphorus "2p" binding energy of *ca.* 1 eV. This is in accord with the old concept of high "polarizability" (Fajans) of sulfur and selenium.

When going from $(C_6H_5)_3P$ to $(C_6H_5)_3PS$, there is an increase of 1.6 eV; whereas, when going from $(C_6H_5S)_3P$ to $(C_6H_5S)_3PS$, there is a decrease of *ca.* 1 eV.

The observed phosphorus "2p" binding energy of 133.5 for $(C_6H_5)_2P(O)OH$ is consistent with the value of 133.5, calculated by taking one-third of the sum consisting of twice the binding energy of $(C_6H_5)_3PO$ plus the binding energy of $(C_6H_5O)_3PO$. This means that the phosphorus "2p" binding energies in phosphoryl compounds, $OP\!<$, might be treated in terms of additive group contributions. The shift of $(C_6H_5)_2P(O)[N(CH_3)_2]$ is in accord with this idea if the group contribution of a nitrogen substituent were to lie part way (as expected) between those in which carbon or oxygen were the nearest neighbors to the phosphorus.

The values of the binding energy of the oxygen "1s"

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[9] K. Siegbahn in "Beta and Gamma Ray Spectroscopy," Vol. I, K. Siegbahn, Ed., North-Holland Publishing Co., Amsterdam, Chapter III, 1965.

[10] R. Nordberg, U. Gelius, P. F. Hedén, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, *Ark. Kemi*, in press.

[11] See K. Sasse, "Houben-Weyl Methoden der Organischen Chemie," Vol. XII, Parts 1 and 2, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1963–1964, for the uncomplexed compounds.

[12] See G. B. Deacon and B. O. West, *J. Inorg. Nucl. Chem.*, **24**, 169 (1962), for $[(C_6H_5)_3PHgI]_2$ and $[(C_6H_5)_3P]_2HgI_2$.

[13] M. G. King and G. P. McQuillan, *J. Chem. Soc. A*, 898 (1967).

[14] The presumably new compound $[(C_6H_5)_3PO]_2HgI_2$, with mp 115–116° and a satisfactory elemental analysis, was prepared in a reaction of stoichiometric amounts of $(C_6H_5)_3PO$ (0.01 *M*) and HgI_2 (0.005 *M*) in acetone (100 ml) and was crystallized twice from ethyl acetate, in analogy to the work of R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **89**, 262 (1906).

[15] A correction for the contact potential between the aluminum spectrometer and the samples has been made by subtracting the spectrometer work function (assumed to be 3.7 eV) from each measured binding energy. For a study of the work function of a spectrometer identical with ours, see A. Fahlman, S. Hagström, K. Hamrin, R. Nordberg, C. Nordberg, and K. Siegbahn, *Ark. Fys.*, **31**, 479 (1966).

[16] M. Pelavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.*, **74**, 1116 (1970).

[17] J. R. Blackburn, R. Nordberg, F. Stevie, R. G. Albridge, and M. M. Jones, *Inorg. Chem.*, **9**, 2374 (1970).

[18] The investigators of ref 16 arbitrarily chose 4.0 eV as the correction due to the spectrometer work function. We use the value 3.7 which was *measured*[15] on a similar spectrometer made in the same shop in Sweden. Repeated measurements of the work function over a period of years by the Siegbahn group have shown that the value of 3.7 eV is quite constant with time. It should be noted in Table I that the difference between our numbers and those from ref 16 is always close to the difference in the work functions used for the two different spectrometers so that we suggest that the correction for the Berkeley instrument should be taken as 3.7 rather than 4.0 eV, a change which ought to make their results directly comparable with the bulk of the literature, which has come from the Swedish workers (K. Siegbahn, *et al.*).

TABLE I: EXPERIMENTAL RESULTS ON INNER-SHELL-ELECTRON BINDING ENERGIES (eV)

No.	Compd[a]	P (2p)	O (1s)	S (2p)	Se (3p)
1	$(C_6H_5)_3P$:	131.1			
	(130.6[b])	131.4			
	(131.9 ± 0.4[c])	131.8			
		131.0			
		131.4			
		Av 131.3 ± 0.3			
2	$(C_6H_5)_3PO$	132.7	530.7		
	(132.7[b])	133.1	531.8		
	(132.9 ± 0.1[c])	132.6	531.9		
		132.6	530.7		
		133.0	Av 531.3 ± 0.7		
		Av 132.8 ± 0.2			
3	$(C_6H_5)_3PS$	132.7		163.0	
	(132.3[b])	133.0		162.1	
		132.9		163.0	
		132.9		Av 162.7 ± 0.5	
		Av 132.9 ± 0.1			
4	$(C_6H_5)_3PSe$	132.7			160.1
		132.9			160.7
		133.0			160.5
		133.2			161.7
		133.3			161.2
		Av 133.0 ± 0.2			Av 160.8 ± 0.6
5	$(C_8H_{17})_3PO$	132.4	530.4		
		132.8	531.3		
		132.5	531.7		
		132.5	Av 531.1 ± 0.7		
		Av 132.6 ± 0.2			
6	$(C_6H_5\underline{O})_3PO$	135.4	533.6		
	(134.2[b])	134.3	533.8		
		135.1	533.8		
		Av 134.9 ± 0.6	Av 533.7 ± 0.1		
7	$(C_6H_5O)_3PS$	134.8	533.1	163.0	
		135.4	533.6	162.9	
		134.7	533.7	Av 163.0 ± 0.1	
		134.8	Av 533.5 ± 0.3		
		Av 134.9 ± 0.3			
8	$(C_6H_5O)_3PSe$	134.1	532.4		160.9
		134.7	532.8		
		134.2	533.9		
		135.1	533.0		
		Av 134.5 ± 0.5	Av 533.0 ± 0.6		
9	$(C_6H_5S)_3P$	134.8		163.5	
	(134.4[b])	134.4		164.0	
		134.1		163.8	
		Av 134.4 ± 0.4		Av 163.8 ± 0.3	
10	$(C_6H_5\underline{S})_3PS$	134.1		163.6	
		133.0		163.9	
		132.9		163.5	
		Av 133.3 ± 0.7		Av 163.7 ± 0.2	
11	$\{[(C_6H_5)_3P]HgI_2\}_2$	131.7			
		131.7			
		131.1			
		Av 131.5 ± 0.3			
12	$[(C_6H_5)_3P]_2HgI_2$	130.8			
		131.1			
		131.3			
		Av 131.1 ± 0.3			
13	$[(C_6H_5)_3PO]_2HgI_2$	132.8	532.2		
		133.1			
		132.8			
		Av 132.9 ± 0.2			
14	$\{[(C_6H_5)_3PS]HgI_2\}_x$	131.8			
	$x = 2$ (?)	131.5			
		132.2			
		Av 131.8 ± 0.4			
15	$[(C_6H_5)_3PSe]HgI_2$	132.3			
		132.2			
		132.7			
		Av 132.4 ± 0.3			
16	$(C_6H_5)_2P(O)OH$	133.9	532.0		
		133.6	532.5		
		133.0	533.0		
		Av 133.5 ± 0.5	Av 532.5 ± 0.5		
17	$(C_6H_5)_2P(O)N(CH_3)_2$	133.7	531.3		
		133.0	531.6		
		132.6	532.7		
		Av 133.1 ± 0.6	Av 531.9 ± 0.7		

[a] Values for the phosphorus "2p" binding energies obtained by other investigators are shown in parentheses. [b] M. Pelavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.*, **74,** 1116 (1970). [c] J. R. Blackburn, R. Nordberg, F. Stevie, R. G. Albridge, and M. M. Jones, *Inorg. Chem.*, **9,** 2374 (1970).

electron are seen to be in the neighborhood of 531.2 for the phosphoryl oxygen (see compounds 2, 5, and 17 in Table I) and 533.4 for the phenoxyl group (no. 7, 8, and also 6). A similar but smaller trend is seen for sulfur where the value of the binding energy for the sulfur "2p" electron is *ca.* 162.8 for the thiophosphoryl sulfur (compounds 3 and 7) and 163.8 for the phenylmercapto group (no. 9 and also 10). Compound 6 in Table I exhibits an oxygen "1s" binding energy corresponding to the phenoxyl group since there are three phenoxyls to one phosphoryl oxygen in $(C_6H_5O)_3PO$ and the peak due to the phenoxyl simply swamps out that of the phosphoryl oxygen in the photoelectron spectrum. The same kind of explanation holds for the sulfur "2p" binding energy of compound 10 and the carbon "1s" binding energies of all of the compounds. In both cases the width of the peak at half-height is about 0.6 eV wider than that of a "normal" line and this is equivalent[19] to a peak separation of 0.5 eV. It should be noted that the peak areas correspond to the assignments made here.

Some Pertinent Theoretical Calculations.—In a theoretical study[20] of p_π–d_π bonding in phosphorus compounds, *ab initio* LCAO–MO–SCF calculations were carried out on phosphine and the hypothetical molecule phosphine oxide, using rather small (undoubtedly unbalanced) Gaussian basis sets of (73/52/2) and (731/52/2). For both molecules, the calculations were made by using only s and p orbitals and alternatively by using s, p, and d orbitals on the phosphorus. Thus, we were able in effect to see what would happen if d orbitals were first disallowed and then were permitted (*i.e.*, switched on in some manner). The changes thus calculated in the absolute value of the phosphorus "2p"-orbital energy when going back and forth from PH_3 to OPH_3 and when switching on and off the d orbitals are shown in eq 1. In these calculations the decrease in the

$$\begin{tikzcd}
OPH_3\text{ (no d)} & OPH_3\text{ (with d)} \arrow[l, "1.4\text{ eV}"'] \\
PH_3\text{ (no d)} \arrow[u, "4.7\text{ eV}"'] & PH_3\text{ (with d)} \arrow[l, "0.3\text{ eV}"'] \arrow[u, "3.6\text{ eV}"']
\end{tikzcd} \qquad (1)$$

absolute value of the phosphorus "2p"-orbital energy upon allowing d orbitals is considerably greater for OPH_3 than for PH_3 and this has been shown[20] to be associated with clearly observable p_π–d_π bonding between the phosphorus and the oxygen, bonding which exists as part of the highest occupied molecular orbital. Note that the increase in binding energy when going from PH_3 to OPH_3 is considerably larger than the decrease due to p_π–d_π bonding. However, because of the small basis sets employed in these calculations, the results must be considered as only indicative.

In a different study,[21] SCF calculations were carried out on the phosphorus atom and it was found that adding one d electron to the valence shell of the most stable terms of the various configurations of the P^+ ion causes the absolute value of the phosphorus "2p"-orbital energy to drop by 4–6 eV, whereas adding one p or one s electron causes a larger decrease of 9–12 eV. For example, going from sp^3 to s^2p^3 corresponds to a calculated drop of 12.5 eV; from sp^3 to sp^4, 10.8 eV; and from sp^3 to sp^3d, 4.6 eV. This indicates that increasing or decreasing the charge on the phosphorus by polarization of the σ bonds is about twice as effective per electron as the reverse effect involving p_π–d_π bonding in which unshared pairs of electrons on the substituents are fed into phosphorus d orbitals. Thus, we might interpret the insignificant change in phosphorus "2p" binding energy upon complexing mercuric iodide with triphenylphosphine as a situation in which the effective number of electrons removed from the phosphorus by formation of the P–Hg bond is accompanied by about twice an amount of charge transfer from the mercury to the phosphorus d orbitals. Note that previous work[16] shows that conversion of triphenylphosphine into the derivative $(CO)_4MnP(C_6H_5)_3{}^+Cl^-$ changes the phosphorus "2p" binding energy by only +0.6 eV.

Charge Calculation from ^{31}P Nmr.—On the basis that nuclear magnetic resonance (nmr) shielding of the ^{31}P nucleus may be attributed wholly to the paramagnetic term when the coordinate origin is located at that nucleus, two groups of investigators[22,23] have independently carried out a theoretical interpretation of ^{31}P nmr data. Although the general approach of these two groups was quite similar, one of them[24] included d orbitals in their calculations and carried out an extensive treatment of the overall problem.

According to this treatment,[23,24] the polarity of the σ bonds to the phosphorus (and hence this contribution to the charge on the phosphorus atom) was obtained from Pauling-type electronegativities, using the relationship of Hannay and Smyth.[25] The charge feedback due to p_π–d_π bonding was then calculated from the observed nmr chemical shift with the aid of this information. It should be noted that the amount of π character in the bonds to the phosphorus from such a treatment of ^{31}P chemical shift data is reasonably consistent with values[26] estimated from internuclear distances (X-ray and electron diffraction) and from heats of formation. This interpretation of the nmr data results in an estimation of the charge located in the d_π orbitals of the phosphorus according to the valence-bond treatment—a treatment in which the concept of a "charge" on an atom is clear-cut as compared to molecular orbital theory.

Values of such σ and π contributions to the overall charge on the phosphorus atom are given in Table II for the molecules treated herein. These charge values are probably to be considered as only indicative since they are, of course, subject to all of the error inherent in the Hannay–Smyth approximation as well as in the assumption[23] made in the nmr calculations that the ratio of the expectation value of r^{-1} divided by the mean excitation

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[19] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969, Appendix D.

[20] H. Marsmann, L. C. D. Groenweghe, L. J. Schaad, and J. R. Van Wazer, *J. Amer. Chem. Soc.*, **92**, 6107 (1970).

[21] H. Marsmann, J. R. Van Wazer, and J.-B. Robert, *J. Chem. Soc. A*, 1566 (1970). (Although the calculations in this minimum-basis-set Slater study were carried out with fixed exponents for the inner-shell orbitals, comparison of these phosphorus "2p"-orbital energies with values calculated with optimization of the exponents of all orbitals[6] shows that the error in the "2p"-orbital energy is only a few tenths of 1 eV.)

[22] H. S. Gutowsky and J. Larmann, *J. Amer. Chem. Soc.*, **87**, 3815 (1965).

[23] J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966); **45**, 2916, 2926 (1966).

[24] J. H. Letcher and J. R. Van Wazer, in "P^{31} Nuclear Magnetic Resonance," Interscience, New York, N. Y., 1967, Chapters 2 and 3.

[25] N. B. Hannay and C. P. Smyth, *J. Amer. Chem. Soc.*, **68**, 171 (1946).

[26] J. R. Van Wazer, *ibid.*, **78**, 5709 (1956).

TABLE II

ELECTRONIC CHARGE ON THE PHOSPHORUS ATOM FROM INTERPRETATION OF ^{31}P NMR CHEMICAL SHIFTS

R		R_3P	R_3PO	R_3PS	R_3PSe
C_6H_5	σ	+0.30	+0.58	+0.38	+0.37
	π^a	−0.00	−0.12	−0.05	−0.04
		+0.30	+0.46	+0.33	+0.33
C_6H_5O	σ		+1.17	+0.97	+0.96
	π		−0.45	−0.36	−0.29
			+0.72	+0.61	+0.67
C_6H_5S	σ	+0.27		+0.35	
	π	−0.10		−0.15	
		+0.17		+0.20	

[a] In ref 23 and 24, the numerical values shown for the number of π electrons is effectively the total number of such electrons, not just those associated with the phosphorus. A number of as yet unpublished electron density maps made in our laboratory show that the π bonds to phosphorus are at least as polar as the σ bonds and in the same direction. Therefore the value of the parameter[23,24] $f(v)$ has been set to $f(3) = 0.0055$ and $f(4) = 0.0045$ for these charge calculations in order to include the same π-bond polarity, h_z, as was employed for the σ bonds.

energy is constant for each coordination number exhibited by the phosphorus and, indeed, varies by only a small fixed amount from one coordination number (*e.g.*, R_3P) to another (*e.g.*, R_3PM). However, they do show qualitatively how important the π contribution is to the total charge, particularly for the phenoxyl derivatives.

In each row of Table II the charge per phosphorus is substantially constant and is quite different from that in the other rows. It is also clear that, as the positive charge on the phosphorus calculated for the σ orbitals becomes smaller, the absolute value of the opposing negative charge attributable to the π orbitals also diminishes (*i.e.*, π-bond feedback) so that we can consider that the value of a measured inner-orbital binding energy for phosphorus (and also for other second- and third-row main-group elements) is the result of considerable charge compensation between the σ-bond polarity and the π-bond feedback. This probably explains the difficulties in data interpretation encountered by the authors of the first study[16] of phosphorus "2p" binding energies and is in accord with their suggestion that such measurements should be useful in interpreting p_π–d_π bonding.

The small decrease in phosphorus '2p" binding energy going from $(C_6H_5S)_3P$ to $(C_6H_5S)_3PS$ is now understandable although the rather high values of these two binding energies relative to those of the other compounds is not in agreement with the charges presented in Table II. For the other compounds of Table II, the usual[3] essentially linear relationship of increasing binding energy with increasing electron-withdrawing power (in this case, σ and π together) of the substituents is found. The atomic calculations treated in the preceding section indicate that the effect of the charge due to the σ electrons ought to be considerably different than the effect of the π-electron charge. However, simply multiplying the σ-bond charge by 2 before adding it to the π-bond "charge" turns out not to be an appropriate way of handling the numbers of Table II.

Final Remarks.—Our original hopes that measurements of inner-orbital binding energies might prove to be a useful method for identifying and subtly classifying phosphorus compounds has not worked out, since a vast number of phosphorus derivatives will surely exhibit binding energies in a narrow middle-range band around 133 eV.[16] In other words, X-ray photoelectron spectroscopy will probably never turn out to be as useful to phosphorus chemists as ^{31}P nmr.[24] However, the measurement of inner-orbital binding energies throws new light on the electronic structure of the compounds of second-row elements and this is leading to a valuable reevaluation of chemists' working concepts concerning these matters and to increased efforts toward the practical application of quantum mechanics to chemistry.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
SAINT LOUIS UNIVERSITY, SAINT LOUIS, MISSOURI 63103

The Aminolysis and Basic Hydrolysis of the *O*-Ethylboranocarbonate Ion

BY B. D. HOEWE, L. J. MALONE,*[1] AND R. M. MANLEY

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Aminolysis of the *O*-ethylboranocarbonate ion ($K^+H_3BCOOC_2H_5^-$) occurs in ethanol solution leading to the formation of boranocarbamates. Of special interest is the formation of the ethylenediaminetris(boranocarboxylate) ion. In addition to this work, a study of the kinetics of the basic hydrolysis of potassium *O*-ethyl boranocarbonate in aqueous solution shows that the reaction follows a first-order rate law. Analogy to the isoelectronic monoethylcarbonate ion is indicated.

Introduction

Certain chemical similarities between a borane adduct and an isoelectronic oxygen compound were first demonstrated by Parry and Bissot.[2] This relationship was also shown to apply to carbon monoxide–borane (H_3BCO) and carbon dioxide in the preparation of car-

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[1] Author to whom correspondence should be addressed.

[2] R. W. Parry and T. C. Bissot, *J. Amer. Chem. Soc.*, **78**, 1524 (1956).